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General and Physical Chemistry.

Some Gaseous Spectra: Hydrogen, Nitrogen. By J. S. AMES (*Phil. Mag.* [5], **30**, 48—58).—Exact determinations of the wave-lengths of the line-spectra of hydrogen and nitrogen. The results are tabulated and compared with those of Hasselberg, Cornu, and Deslandres. H. C.

Relations between the Lines of Various Spectra, with special reference to those of Cadmium and Zinc, and a Redetermination of their Wave-lengths. By J. S. AMES (*Phil. Mag.* [5], **30**, 33—48).—The author gives an historical and critical survey of the various theories that have been put forward with regard to supposed relations between the lines of the spectra of different elements. Measurements of the wave-lengths and descriptions of the lines of the zinc and cadmium spectra are given from photographs made by Rowland of the arc spectra. The two spectra consist mainly of groups of three lines, which overlap in the cadmium spectrum; but line for line and group by group the two spectra correspond. The differences of the wave-numbers of the last lines in each of the triplets of the two spectra are practically identical. The differences in wave-numbers between the first and second lines in each triplet are all found to be about 39 for zinc and 117 for cadmium; the differences between the second and third lines are 19 for zinc and 54 for cadmium. The first set of differences is therefore in each case about double the second. The spectrum of magnesium has 10 groups of triplets, but these bear no apparent relation to those of zinc and cadmium. There is, however, one broad reversed line common to the three spectra; in magnesium, at wave-length 2852·2; in zinc, at wave-length 2138·3; in cadmium, at wave-length 2288·1. The differences of the wave-numbers in each magnesium triplet are also nearly constant, being close to 4 and 2. The spectra of calcium, strontium, barium, and mercury also contain triplets, but their number is small in comparison with that of the lines not so included. H. C.

Spark Spectrum of Gadolinium Chloride. By L. DE BOISBAUDRAN (*Compt. rend.*, **111**, 472—474).—With a spark of low intensity, the spectrum of a hydrochloric acid solution of gadolinium chloride consists of many bands and lines; with a more intense spark, the bands disappear, and the spectrum consists of lines only. With a coil of low intensity, and the poles widely separated, the development of the bands is very remarkable.

The following are the more important wave-lengths in the prismatic spectrum with a spark from a coil of high intensity:—

6223, 5827, and 5698, middle points of somewhat strong bands.

5101, 4888, 4617, and 4467, lines at the edges of bands.

5723, 5705, 5686, 5669, 4929, 4908, 4888, 4793, 4633, 4617, and 4467, lines superposed on the bands, or, in some cases, appearing independently of bands. C. H. B.

The Spectroscopical Properties of Russian Oil of Peppermint. By H. ANDRES (*Chem. Centr.*, 1890, ii, 149; from *Pharm. Zeit. Russ.*, **29**, 257—260).—The author has compared the spectroscopical properties of Russian oil of peppermint with those of the English oil, as described by Tichomiroff, and finds that they are almost identical, the only differences being (1) that the black band, which in the case of the English oil appears between 8·5 and 9·5 (D = 10), in that of the Russian oil is somewhat wider, extending from 8·5—10·0; (2) the most highly refractive part of the spectrum, from 14·5 to the ultra-violet end, is quite clear in the case of the English oil, whereas in that of the Russian oil, the blue and violet is darkened.
J. W. L.

Measurement of the Quantity of Light that Enters Water. By P. REGNARD (*Compt. rend. Soc. Biol.* [9], **11**, 289).—A line was suspended in the sea by an anchor at the bottom and a buoy at the top. Along this at distances of 2 or 3 metres from one another were placed tubes filled with equal volumes of hydrogen and chlorine. The amount of hydrochloric acid formed by the combination of the two elements is proportional to the amount of light they receive (Bunsen and Roscoe). These preparations are made one night; the light of the day enters the water in inverse proportion to its depth; the next night the tubes, which are graduated, are examined, and the results coincide very closely with those previously obtained with a selenium pile. W. D. H.

Change of Volume on Mixture of Two Liquids, and its Influence on the Refractive Power. By L. BUCHKREMER (*Zeit. physikal. Chem.* **6**, 161—186).—The author understands by contraction on mixing two substances (dilatation being considered as negative contraction), the expression $\frac{D - D_v}{D}$. D_v is the calculated density the mixture would possess if no contraction took place; D is the observed density of the mixture. A similar expression $\frac{N - N_v}{N}$ represents the "contraction" of the refractive power of two substances on mixing. Pulfrich has stated (*Zeit. physikal. Chem.*, **4**, 562) the following relations between these two magnitudes :—

$$(1.) \ldots\ldots\ldots \quad \frac{N - N_v}{N} = \alpha\frac{D - D_v}{D},$$

$$(2.) \ldots\ldots\ldots \quad \frac{N - N_v}{N} \text{ and } \frac{D - D_v}{D}, \text{ have always the same sign.}$$

(3.) α is scarcely affected by change of wave-length in feebly dispersive substances. Strongly dispersing media exhibit a continual decrease or increase of α from one end of the spectrum to the other.

The author now tests these relations very fully from the experimental standpoint, and finds in almost every case a confirmation of the rules. His results and those of other investigators are contained in numerous tables and curves. J. W.

Secondary Batteries. By J. H. GLADSTONE and W. HIBBERT (*Phil. Mag.*, [5], **30**, 162—170).—The addition of sodium sulphate to the acid solution of an ordinary secondary battery is known to be of considerable advantage to the working of the cell. The authors find that in this case a large proportion of sodium sulphate is formed in close contact with the lead sulphate at the cathode, and they show that this would be favourable to the reduction of the latter substance, as a paste made of equal parts of red lead and lead sulphate is more readily reduced in a solution of normal sodium sulphate than in dilute sulphuric acid. They find also that the presence of sodium sulphate diminishes the local action arising between the acid and different parts of the plates. No indication could be found of the formation of either of Frankland's sub-sulphates of lead on treating litharge with dilute sulphuric acid, and the authors believe the ordinary sulphate of lead to be the substance produced in the voltaic reaction. The high initial E.M.F. observed in a secondary battery when the charging current has just been stopped is shown to be due to inequalities in the acid strength produced by the current. An increase in the strength of the acid surrounding the positive (peroxide) plate is found to take place, and this causes the abnormal E.M.F., which gradually disappears as the strength of the acid is equalised by diffusion. H. C.

Electromotive Force of a Metal in a Series of Electrolytes. By G. MAGNANINI (*Gazz.*, **20**, 308—311).—The following table exhibits the average results of a series of experiments undertaken with the view of ascertaining the variation of the E.M.F. of a metal with the nature of the electrolyte in which it is placed.

The measurements were made by Poggendorff's compensation method, using the capillary electrometer.

The difference of potential at the extremity of the measuring rheostat was maintained at 1 volt, and the metals were successively immersed in each of the series of electrolytes and compared with zinc or cadmium, or lead, in normal sulphuric acid; the E.M.F. was calculated in hundredths of a volt with respect to zinc in sulphuric acid.

Electrolyte, strength of solution in grams per litre.	Zn.	Cd.	Pb.	Sn.	Cu.	Ag.
$\frac{1}{2}$ mol. H_2SO_4	0·00	36·6	51·3	51·3	100·7	121·3
1 ,, NaOH	−32·1	19·5	31·8	0·2	80·2	95·8
1 ,, KOH	−42·5	15·5	32·0	−1·2	77·0	101·0
$\frac{1}{2}$,, Na_2SO_4	1·4	35·6	50·8	51·4	101·3	120·9
1 ,, $Na_2S_2O_3$	−5·9	24·1	45·3	45·7	38·8	64·8
1 ,, KNO_2	11·8 (1)	31·9	42·6	31·1	81·2	105·7
1 ,, $NaNO_2$	11·5	32·3	51·0	40·9	95·7	114·8
$\frac{1}{2}$,, K_2CrO_4	23·9 (1)	42·8	41·2	40·9	94·6	121·0
$\frac{1}{2}$,, $K_2Cr_2O_7$	72·8	61·1	78·4	68·1	123·6	132·4
$\frac{1}{2}$,, K_2SO_4	1·8	34·7	51·0	52·4	101·1	123·6
$\frac{1}{2}$,, $(NH_4)_2SO_4$	−0·5	37·1	53·5	57·6 (1)	101·5	125·7
$\frac{1}{4}$,, $K_4FeC_6N_6$	−6·1	33·6	50·7	41·2	(1)	87·8
$\frac{1}{6}$,, $K_6Fe_2(CN)_{12}$	41·0 (2)	80·8	81·2	130·9	110·7	124·9
1 ,, KCNS	−1·2	32·5	52·8	52·7	52·5	72·5
1 ,, $NaNO_3$	4·5	35·2	50·2	49·0	103·6	114·6
$\frac{1}{2}$,, $Sr(NO_3)_2$	14·8	38·3	50·6	48·7	103·0	119·3
$\frac{1}{8}$,, $Ba(NO_3)_2$	21·9	39·3	51·7	52·8	109·6	121·5
1 ,, KNO_3	(1)	35·6	47·5	49·9	104·8	115·0
$\frac{1}{5}$,, $KClO_3$	15 to 10·0 (1)	39·9	53·8	57·7	105·3	120·9
$\frac{1}{6}$,, $KBrO_3$	13 to 20·0 (1)	40·7	51·3	50·9	111·3	120·8
1 ,, NH_4Cl	2·9	32·4	51·3	50·9	81·2	101·7
1 ,, KF	2·8	22·5	41·1	50·8	61·3	61·5
1 ,, NaCl	—	31·9	51·2	50·3	80·9	101·3
1 ,, KBr	2·3	31·7	47·2	52·5	73·6	82·4
1 ,, KCl	—	32·1	51·6	52·6	81·6	107·6
$\frac{1}{2}$,, Na_2SO_3	−8·2	28·7	41·0	51·0	68·7	103·7
(3) NaOBr	18·4	41·6 (1)	73·1	70·6 (1)	89·9	99·7
1 mol. $C_4H_6O_6$	5·5	39·7	61·3	54·4 (2)	104·6	123·4
$\frac{1}{2}$,, ,,	4·1	41·3	61·6	57·6	110·9	125·7
$\frac{1}{2}$,, $C_4H_4KNaO_6$	−7·9	31·5	51·5	42 to 47	100·8	119·7

(1) Not constant. (2) After a time. (3) A quantity of bromine was used corresponding to NaOH = 11.

It is noticeable that the ordinary salts give values in general not far removed from each other, the more important deviations occurring in electrolytes which may be assumed to have an exceptional action on the metal; oxidising agents, for instance, increase and reducing agents diminish the E.M.F. The differences also depend on the nature of the metal.

S. B. A. A.

Electrical Resistance of Metals. By H. Le Chatelier (*Compt. rend.*, **111**, 454—458).—The author has previously shown that measurements of the electrical resistance of metals may be applied to the study of molecular changes. When a metal undergoes no molecular change below its melting point, the variation in electrical resistance is a linear function of the temperature. The following numbers give the resistance in ohms of wires 1 mm. in diameter :—platinum, 0·140 + 0·000325t; platinum + 10 per cent. of rhodium, 0·335 + 0·000350t; copper, 0·032 + 0·000101t; copper + 10 per cent. of tin, 0·150 + 0·000109t; copper + 20 per cent. of nickel, 0·420 + 0·000110t; silver, 0·023 + 0·000105t.

Copper, silver, and their alloys with other metals, have practically the same coefficient of variation (approximately 0·000105), that of platinum and its alloys being three times as great. As a general rule, the addition of a small quantity of a foreign metal displaces the curve of resistance parallel with itself.

When silver is heated in oxygen, its curve of resistance remains perfectly rectilinear, and its melting point and mechanical properties are not altered. When, on the other hand, it is heated in hydrogen, all its properties alter above 650°; the resistance increases more rapidly than in oxygen and the metal after cooling melts at 915° and is so brittle that a wire 0·25 mm. in diameter cannot be bent without breaking. The metal has a dull appearance resembling that of palladium hydride, but the quantity of hydrogen absorbed by the silver at a dull-red heat is not sufficient to form a definite compound, and the metal retains no hydrogen after being cooled.

Metals similar to iron (Abstr., 1890, 549) show variations in the temperature coefficient, but no variations in the absolute value of the resistance similar to those observed at the melting point.

Zinc undergoes a molecular change at 360°; brass containing 38 per cent. of zinc, at 720°; and an alloy of copper 70 pts., nickel 18 pts., and iron 11 pts., at 690°. In the case of brass, the molecular change is accompanied by a considerable absorption of heat.

Some alloys show gradual molecular changes recalling the changes in the equilibrium of saline solutions; the change does not take place suddenly, but gradually, between certain limits of temperature. A somewhat siliceous aluminium bronze showed a change between 550° and 650°; German silver and copper-nickel alloys showed a change between 300° and 500°. In all experiments of this kind, it is essential that the pieces of alloy or metal used should be very carefully annealed. The resistance of German silver resistance coils alters with time, because the coils are in a partially tempered condition, but gradually anneal under the influence of slight variations in temperature, mechanical disturbances, &c.

In the case of iron and nickel alloys, the effect of an increase of temperature is not immediately reversed by cooling; the metal only acquires its original resistance when cooled to the surrounding temperature.

Iron, nickel, and their alloys, at temperatures above the point of transformation, have a temperature coefficient of similar magnitude to that of platinum and the allied metals, whilst below the point of transformation the resistance of iron, nickel, and their alloys increases much more rapidly than that of the platinum metals. C. H. B.

Electrical Conductivity of Salts in the Bunsen Flame. By S. Arrhenius (*Sitzungsber. Akad. Wiss., Wien*, **99**).—An ordinary Bunsen burner was fed by gas and air, both under constant pressure.

The air current passed through a spray of solution of the salt to be examined. The concentration of this solution determined the amount of salt which passed into the flame. Two platinum plates were introduced into the flame at a distance of 0·56 cm. from each other, and served as electrodes. The circuit contained a battery of 40 Clark elements and a Wiedemann galvanometer. The resistance of the flame was very great compared with that of the remainder of the circuit, so that the deflection of the galvanometer measured the conductivity of the flame.

The relation between E.M.F. e and intensity i was found to be $i = kf(e)$, where k is a constant and f a function which remains the same for all salts at all concentrations.

Only at values below 0·2 Dan. does Ohm's law hold for conduction in the Bunsen flame. The conductivity of the salt in the flame (that is, the total conductivity minus that of the flame itself) is proportional to the square root of the concentration. This was shown to hold good with great approximation for 16 different salts. At extreme dilutions, the conductivity increases somewhat more rapidly. All potassium salts conduct equally well: the same holds true for sodium and for lithium salts.

The conductivity of the chlorides of the alkali metals increases with their molecular weight. Salts of H, NH_4, Mg, Zn, Cd, Cu, Fe, Ni, Co, Al, Cr, Mn, and Sn do not seem to conduct. Salts of barium, calcium, and strontium conduct by convection of small solid particles, but probably also electrolytically. The difference of potential between two metals in a Bunsen flame containing saline vapours is of the same sign and order of magnitude as when the same metals are immersed in an electrolytic liquid. On the whole, salts in a Bunsen flame behave like a feebly dissociated electrolyte, the chief point of difference being that Ohm's law is not obeyed for large E.M.F.'s.

J. W.

Aqueous Solutions of Double Salts. By W. KISTIAKOFFSKY (*Zeit. physikal. Chem.*, **6**, 97—121).—It has been proposed by Ostwald to confine the term "double salt" to such compound molecules as are decomposed into their compounds on dissolution, and to use the designation "complex salt" for those which undergo no decomposition. The present paper is a contribution to this classification, the author having investigated a large number of solutions containing salts in molecular proportions. From the electrical conductivity of solutions of given strength, it is possible to obtain information as to the number of ions conducting the electricity, and consequently conclusions may be drawn as to whether the double salts are decomposed into simple salts on dissolution or not. The following substances were found by this means to be (undecomposed) complex salts:—$KAg(CN)_2$, $K_2Ni(CN)_4$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Cr(C_2O_4)_3$, $Ag_3Cr(C_2O_4)_3$, $(NH_4)_3Fe(C_2O_4)_3$. Double sulphates such as $(NH_4)_2SO_4,CuSO_4$ and the alums are completely decomposed in solution. If the salt $Ag_3Cr(C_2O_4)_3$ were a double salt, then the silver and the chromium, on electrolysis, would travel to the same electrode; if, on the other hand, it is a complex salt, the metals will travel in opposite directions. From quantitative experiments, the author finds that the latter alternative is correct, and that the ions of silver chromoxalate are $3Ag$ and $Cr(C_2O_4)_3$.

Another mode of attacking the question is given by the depression of the freezing point; and this method is found to yield precisely similar results. The complex salts are found to obey Arrhenius's law of electrolytic dissociation; the double salts, on the contrary, give too large values for the coefficient *i*.

The author concludes that when a simple salt tends by itself to form compound molecules in solution, it has the power to form compound molecules with other salts. J. W.

Isomerism of the Metaphosphates. By G. Tammann (*Zeit. physikal. Chem.*, **6**, 122—140).—From an investigation of the electrical conductivity and the freezing point of solutions of the various metaphosphates, the author, by interpreting his results in the light of the dissociation theory, seeks to draw conclusions as to the size of the molecules of these salts.

It would seem that the salts which have hitherto gone by the name of dimetaphosphates in reality have the formula $M_3P_3O_9$, whilst those known as trimetaphosphates correspond with the formula $M_2P_2O_6$.

All the sodium metaphosphates, on being heated, pass into the easily soluble variety known as Graham's salt. This, however, is not a uniform substance, as different specimens exhibit electrical conductivities varying by as much as 20 per cent. On precipitation with silver nitrate, it gives a crystalline silver salt and a heavy liquid. The crystalline salt, treated with sodium chloride, gives a substance of the constitution $Na_6(P_3O_{18})$. Graham's salt is probably a mixture of this with $Na_4(Na_2P_3O_{18})$ and $Na_5(NaP_3O_{18})$.

The parts of the preceding formulæ within brackets represent the anion formed on solution in water.

There are apparently also salts of the composition $Na_3(Na_3P_3O_{18})$,

$$Na_2(Na_4P_3O_{18}),\ K_2(Na_4P_3O_{18}),\ K_2(Ag_4P_3O_{18}),\ Ag_4(Na_2P_3O_{18}),$$

$Ag_5(NaP_3O_{18})$, $(NH_4)_5(NaP_3O_{18})$, and three different insoluble sodium metaphosphates. J. W.

Electrification of Effluvia from Chemical or from Voltaic Reactions. By J. Brown (*Phil. Mag.* [5], **30**, 21—30).—Experiments are described, showing that when gas is evolved in a chemical or voltaic reaction, the effluvium, that is, the gas or something carried up with it, is usually, as shown by Enright (*Phil. Mag.* [5], **29**, 56), electrically charged. No electrification is, however, produced by simple effervescence unaccompanied by chemical change. The sign of the electrification is influenced by the kind of chemical or voltaic action taking place, and does not seem to be due to any contact effect, the conclusion by Enright that nascent hydrogen or other gases become positively electrified by contact with acids, and negatively by contact with salts in solution, being incorrect. When the effluvium is that given off from zinc dissolving in hydrochloric acid (taken as a typical experiment), and consists of hydrogen accompanied by foggy matter, it is not decided whether the charge is given originally to the gas or the fog particles, although the balance of evidence inclines towards the latter view. The fog in question seems to be formed at, or nearly at, the same time and place as the gas; and the nature of its charge is, therefore, possibly influenced by the voltaic conditions there present. The gas, or effluvium, from the decomposition of a liquid by a current from the poles of a separate battery immersed in it appears also to be electrified. H. C.

Changes of Property in Amalgams by Repeated Fusion. By G. GORE (*Phil. Mag.* [5], **30**, 228—230).—It is well known that various alloys undergo a change of properties by repeated melting and cooling. This the author finds to be the case with an amalgam composed of one part by weight of cadmium to four of mercury, for the E.M.F. of a voltaic couple formed by such an amalgam and a strip of platinum in a solution composed of one part by weight of common salt to 100 of distilled water is found to be reduced by repeated fusion, until after about the fifth fusion it becomes constant. At the same time, the amalgam alters in volume, for determinations of the specific gravity after the first and sixth fusions gave 12·5438 and 12·6190 at 14·5°. A similar change was found to take place spontaneously in the freshly-prepared amalgam, a diminution in the E.M.F., measured as above, taking place during the first few days, and clearly indicating a spontaneous molecular change in the amalgam. The author concludes that this amalgam, by the act of fusion and subsequent cooling, and by spontaneous change, suffers a loss of molecular motion, potential heat, chemical activity, and voltaic energy, diminishes in volume, and becomes less corrodible in a solution of sodium chloride. The changes appear to be permanent. H. C.

The Rise of the Zero Point in Thermometers of Jena Glass. By F. ALLIHN (*Zeit. anal. Chem.*, **29**, 381—388).—Eight of the thermometers which were under observation a year ago (Abstr., 1889, 1041), and which have not been used in the interval, have again been examined. In some of them no further rise in the zero point has taken place, and in none has it exceeded 0·02°, thus making the total rise only 0·03—0·04° in a period of four years dating from a few weeks after manufacture.

The rise which occurs when a thermometer is for a long time kept at a high temperature is with Jena glass only about half that of ordinary Thuringian glass. It tends to a limit which is practically reached by 30 hours' heating at 300°. The author accordingly recommends that all such thermometers should be so heated before graduating. M. J. S.

The Expansion of Water and other Liquids. By S. U. PICKERING (*Phil. Mag.*, **30**, 400).—Some determinations made by the author led him to examine the values for the expansion of water given by Hagen, Jolly, Kopp, Pierre, Rosetti, Mathiessen, and Despretz, with the view of ascertaining whether they indicated any sudden changes in the rate of expansion. Plotting the differential coefficients obtained directly from the experimental values was the method employed. The results obtained by the majority of these physicists indicated three changes: at 9—11°, at 17—20°, and at 50—60° respectively; but they were not sufficiently marked to afford absolute proof of their existence, especially in the absence of confirmation from a similar study of other properties. Pierre's results with 11 other liquids were examined in the same way: the majority of them showed changes similar to those shown by water, and, as they occurred at different temperatures, the idea that they were due to irregularities in the expansion of glass is precluded. The first differential appears in most cases to be a straight line. S. U. P.

Pressure variations of certain High Temperature Boiling Points. By C. Barus (*Phil. Mag.* [5], **29**, 141—157).—The author describes a method for the calibration of thermo-couples by aid of boiling points, and then applies it in measuring the vapour tensions of sulphur, zinc, cadmium, and bismuth. It is found that the tensions of saturated vapour from 40 to 760 mm., in terms of temperature, can be expressed by Dupré's equation $\log p = \mathrm{A} - \mathrm{B}/\theta - \mathrm{C} \log \theta$, the best agreement being obtained by keeping C constant throughout, and A variable. The latter step is suggested by assuming that for any two substances S and S′, the boiling points θ and θ', corresponding with a given pressure p, will follow the relation $\mathrm{B}/\mathrm{B}' = \theta/\theta' = 1/n$, where n is constant for the given pair of substances. This is virtually the principle of Groshans, and postulates a fundamental equation of the form given above, from which all others are derived by substitution as follows:—

$$\begin{aligned}\mathrm{Log}\, p &= \mathrm{A} - \mathrm{B}/\theta - \mathrm{C} \log \theta,\\ &= \mathrm{A} - n\mathrm{B}/n\theta - \mathrm{C} \log n\theta + \mathrm{C} \log n,\\ &= \mathrm{A}' - \mathrm{B}'/\theta' - \mathrm{C} \log \theta'.\end{aligned}$$

Making the above assumption, the following values have been obtained for the constants in the cases investigated, and enable the results to be calculated very nearly within the error of experiment. The numbers for water have been added from Dupré and Bertrand's observations.

	A.	B.	C.
Water	19·324	2795	3·868
Sulphur	19·776	4458	3·868
Cadmium	20·63	7443	3·868
Zinc	20·98	8619	3·868
Bismuth	21·51	12862	3·868

H. C.

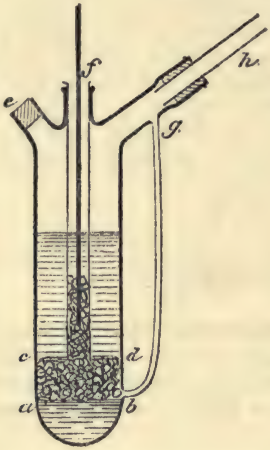
Raoult's Ebullioscope. By R. Lespieau (*Bull. Soc. Chim.* [3], **3**, 855—858; compare Abstr., 1889, 7).—When f is the maximum vapour tension of a liquid whose molecular weight is M_1, f' the maximum vapour tension of a solution in the given liquid of P grams of a substance whose molecular weight is M, then

$$\frac{100\text{ M}}{\text{PM}_1} \cdot \frac{f - f'}{f'} = \text{K},$$

K being a constant whose value for water, chloroform, benzene, carbon bisulphide, and ether is 1—1·05. For acetic acid, an abnormal value 1·61 obtains.

If t is the boiling point of the solvent under pressure f_1, and t' and f_2 the corresponding values for the solution, then the maximum tension of the solvent at t'° is f_1 plus the augmentation of vapour tension suffered by it in passing from t° to t'°, and if the barometer is constant throughout the experiment, f of the formula above given becomes $f = f_1 + n(t' - t)$, where n is the rate of increase in vapour tension for the solvent at temperatures near t; in the case of water, this is 27 mm. for temperatures near 100°.

To determine the value of $t' - t$, the following apparatus is used by Raoult:—



To ensure a regular heating of the solvent, which is boiled in the vessel shown in the figure, some mercury, covered by 2 cm. of coarsely-powdered glass, is placed at the base, and the condensed vapour is returned from the condenser *h* by a tube *g* entering the vessel below the glass. The bulb of the thermometer (which is graduated in two hundredths of a degree) is immersed in mercury contained in the tube *f*, which, after introduction into the apparatus, is read until the heating of the vessel determines a constant temperature. After a slight cooling, the substance M is introduced by the opening *e*, and the apparatus is further heated to determine t'.

Although this method is less sensitive than the cryoscope process, yet concentrations up to 20 per cent. may be employed, the only condition being that the substance should boil at least 150° higher than the solvent. T. G. N.

Thermochemistry of Fats and Fatty Acids. By F. STOHMANN and H. LANGBEIN (*J. pr. Chem.* [2], **42**, 361—382; compare Abstr., 1885, 857).—The authors have redetermined the heats of combustion of several fats and fatty acids, using the calorimetric bomb and performing the combustions in oxygen at 24 atmospheres pressure.

The mean heat of combustion at constant pressure of 1 gram of various samples of fat is 9500 cal.; that of butter is 9231·3 cal. The heat of combustion is less when the fat is rancid, but the variation differs greatly in different fats; in butter it is almost the same.

In the following table the second column gives the heat of combustion per molecule at constant pressure, and the third column the heat of formation (C = 94, H = 69):—

	Cal.	Cal.
Erucic acid	3297·2	219·8
Brassidic acid	3290·1	226·9
Dierucin	6979·5	474·5
Dibrassidin	6953·7	500·3
Trierucin	10265·5	636·5
Tribrassidin	10236·0	682·9
Lauric acid	1771·8	184·2
Myristic acid	2085·9	196·1
Trilaurin	5707·0	512·0
Trimyristin	6650·5	546·5
Behenic acid	3338·3	247·7
Behenolic acid	3255·1	192·9
Dihydroxybehenic acid	3235·5	350·5

The formation of glycerides from glycerol and acids is exothermic in the six cases investigated by the authors. A. G. B.

Determination of Specific Gravity of Solids. By O. KLEINSTÜCK (*Chem. Zeit.*, **14**, 233—234).—A narrow-necked, pear-shaped glass vessel furnished with a funnel-shaped mouth, a hook below and a mark on the neck, is floated in water: the substance of which the gravity is to be ascertained is attached to the hook, either directly or through the intervention of a pan or wire gauze holder, then by pouring in water the vessel is caused to sink to the mark; the substance is now removed, and the vessel again caused to sink to the mark, this time noting the quantity, by weight or volume, of water required for the purpose; the sp. gr. is calculated from this number. For gravities below unity the weighted vessel is first adjusted to the mark; then the displacement caused by attaching the lighter substance is measured by the water required for the readjustment. D. A. L.

Dissociation of Selenium Chlorides. By W. RAMSAY (*Bull. Soc. Chim.* [3], **3**, 783—784; compare Trans., 1884, 62; Abstr., 1890, 558).—The author disputes the statement of Chabrié, that selenium dichloride boils towards 300° without decomposition, and gives experimental proof of its dissociation at 130—170°. In reference to the sublimation of selenium tetrachloride in a sealed tube at 350°, it is conceivable that the substance is not heated above its normal volatilisation point at the normal pressure (190°) before subliming, and this conception is confirmed by the facts observed by Chabrié himself, that the tetrachloride dissociates at 300° into dichloride and chlorine, and that this latter is also dissociated into selenium and chlorine, for selenium is always found in the tube after the sublimation of the tetrachloride. T. G. N.

New Periodic Property of the Elements. By W. SUTHERLAND *Phil. Mag.* [5], **30**, 318—323).—In solids, the molecules may be assumed to vibrate about a mean position, and at some characteristic temperature each solid to have a period of vibration characteristic of its molecule. The most likely temperature for which this would be the case would be the melting point, when the vibratory motion of the molecule just breaks down. Suppose a molecule of mass M and mean specific heat C, heated up from rest at absolute zero to its melting point T. It receives heat MCT proportional to its kinetic energy $\frac{1}{2}Mv^2$, where v is the velocity of the molecule at the melting point. By Dulong and Petit's law, MC is approximately constant for the elements, so that v is proportional to $\sqrt{T/M}$. Knowing thus the velocity of vibration, from its length L its time or period L/v is obtainable. Let d be the density of the substance, then M/d represents the volume occupied by the molecule; and if a is the mean coefficient of linear expansion of the substance between absolute zero and T, then $aT(M/d)^{\frac{1}{3}}$ represents the increase in the linear dimensions of the space occupied by a molecule when heated from zero to T, and therefore represents the length or amplitude of the vibration just as the molecule is going to leave the vibratory state characteristic of the solid. Hence the periodic time p of the molecule at the melting point is proportional to $aT(M/d)^{\frac{1}{3}}\sqrt{MCT/M}$. The value of a is unknown for many of the elements, but the author has found an empirical equation by means of which it may be determined, namely, $aTM^{\frac{1}{6}} = \text{const.}$, the constant being about 0·045 for all metals except antimony, bismuth, and tin. Substituting this value and dropping all constants from the formula, p becomes proportional to $(M/d)^{\frac{1}{3}}M^{\frac{1}{3}}/\sqrt{T}$.

Taking M as the atomic weight, and calculating the period of vibration by the above formula, we get for the lithium family:—

Li.	Na.	K.	Rb.	Cs.
0·21	0·43	0·66	0·96	1·23

or numbers in the ratio 1, 2, 3, 4·5, 6; and for the next group of the periodic law,

Be.	Mg.	Ca.	Sr.	Ba.
0·35	0·70	1·04	1·62	1·88

numbers in the ratio, 1, 2, 3, 4·5, and 5·3. Copper and silver have periods 0·21 and 0·30, which are nearly as 2 to 3, and involve the same fundamental constant as the main family; and zinc and cadmium have periods 0·32 and 0·47, in which the same peculiarity occurs.

The periods of the other elements do not exhibit such marked relations, but the following series is remarkable:—

Mn.	Fe.	Co.	Ni.	Ru.	Rh.	Pd.	Os.	Ir.	Pt.
0·16	0·16	0·16	0·17	0·21	0·20	0·23	0·23	0·25	0·27

The periods of vibration of compounds are also considered, and it is found that p for each molecule is a sum of parts due to each atom in the molecule. H. C.

Approximate Algebraic Expression of the Periodic Law. By T. Carnelley (*Phil. Mag.* [5], **29**, 97—113).—The atomic weights of the elements, arranged according to the periodic law, may be represented by the formula $A = c(m + v^{\frac{1}{x}})$ where A is the atomic weight, c a constant, m a member of an arithmetical progression depending on the series to which the element belongs, and v the maximum valency of the group of which the element is a member. After numerous trials, the best results have been obtained when $x = 2$ and $m = 0, 2\frac{1}{2}, 5, 5 + 3\frac{1}{2}, 5 + 2(3\frac{1}{2}), 5 + 3(3\frac{1}{2})$, &c., for each series respectively from series ii to xii of Mendeléef's table, so that m is a member of an arithmetical progression in which the common difference is $3\frac{1}{2}$, except in the first two terms, where the common difference is $2\frac{1}{2}$.

The calculated values for c vary from 6·0 (carbon) to 7·2 (selenium), with a mean value of 6·64. The high values of c occur mainly with elements belonging to the higher groups (namely, 5, 6, and 7), whilst low values belong to the lower groups (1, 2, and 3). The greatest extremes occur in group 4, Ti and Ge being high, C and Si low. The equation $A = c(m + \sqrt{v})$ becomes $A = c(m + 1)$ for elements of the first group, so that for potassium $c(m_4 + 1) = 39$, and for silver $c(m_7 + 1) = 107·7$. If x represents the common difference in the arithmetical progression, then $m_7 = m_4 + x$, and $107·7 = c(m_4 + 1) + 3xc = 39 + 3xc$, from which $xc = 22·90$. In the same way, by taking different pairs of elements of group 1, different values for xc are obtained, the mean of which is 22·85, or "the difference between the atomic weights of any two elements in group 1 (from series iv upwards), divided by the difference between the number of the series to which each element belongs gives a constant, or $\frac{B - A}{y - x}$ = const. = 22·85 where x and y are the numbers of the series to which the elements A and B respectively belong." The constant 22·85 is very nearly identical with the atomic weight of sodium (22·99). Atomic weights calculated from the equation $A = c(m + \sqrt{v})$ agree more closely with the observed values than do those determined by Dulong and Petit's law. Specific volumes calculated from the volumes so obtained also agree well with the usual values. The greatest discrepancies occur at the end of series iv, v, and vii, and at the beginning of series xi.

In the equation $A = c(m + \sqrt{v})$, the constant c has a mean value of 6·6, which suggests the constant 6·4 of Dulong and Petit's law. If c represents the atomic heat, then atomic weight = atomic heat × $(m + \sqrt{v})$ = atomic weight × specific heat × $(m + \sqrt{v})$, or 1 = specific heat × $(m + \sqrt{v})$, whence specific heat $= \dfrac{1}{m + \sqrt{v}}$. Specific heats calculated in this way agree closely with the observed values, especially if specific heats at high temperatures be taken, since in this case the constant 6·4 of Dulong and Petit's law approximates to 6·6.

The value m in the equation $A = c(m + \sqrt{v})$ is the member of an arithmetical progression, and is a whole number for the even series and a number and a half for the odd series, in this way corresponding with the well-known difference between the series. Again, the common difference is $2\frac{1}{2}$ for the first three members, but is $3\frac{1}{2}$ afterwards. This accords with Mendeléeff's statement, that the second and third series are more or less exceptional. H. K. T.

Osmotic Pressure. By M. Planck (*Zeit. physikal. Chem.*, **6**, 187—189).—The author has in previous memoirs deduced the laws regulating the vapour pressure and freezing point of solutions from thermodynamical principles. In this paper he shows that, given a membrane between a solution and the pure solvent, permeable only to the latter, it is possible, without making any assumptions as to the nature of osmotic pressure, to deduce from the same general conditions of equilibrium the laws discovered by van't Hoff.

The final equation he obtains is $p - p' = n\theta/V$. V is the volume of the solution, θ its absolute temperature, n the number of molecules of the dissolved substance, p the pressure in the solution, and p' the pressure in the solvent; $p' - p$ is thus the osmotic pressure, which, as the equation shows, is inversely proportional to the volume (Boyle's Law), directly proportional to the absolute temperature (Charles' Law), and further proportional to the number of dissolved molecules (Avogadro's Law). J. W.

Inorganic Chemistry.

Properties of Liquid Chlorine. By R. Knietsch (*Annalen*, **259**, 100—124).—The author has made a series of determinations of the vapour tension of chlorine from −88° to 146°, and of its specific gravity at temperatures ranging from −80° to 77°; the results are given in tables and as curves, and the methods and apparatus employed are fully described with the aid of various diagrams.

The critical temperature of chlorine was found to be 146°.

F. S. K.

Simple and Rapid Evolution of Pure Gases. By H. Bornträger (*Zeit. anal. Chem.*, **29**, 412; see Abstr., 1890, 849).—The production of chlorine from a mixture of bleaching powder and sodium hydrogen sulphate was patented by O. Stüber, on April 5th, 1890.

M. J. S.

Atomic Weight of Fluorine. By H. MOISSAN (*Compt. rend.*, **111**, 570—572).—Sodium carbonate, prepared by the ammonia process from carefully purified sodium chloride, was converted into fluoride by the action of hydrofluoric acid from potassium hydrogen fluoride. The sodium fluoride was then converted into sulphate. The results of five determinations varied between $F = 19·04$ and $F = 19·08$ ($Na = 23·05$, $S = 32·074$, and $O = 16$).

Calcium fluoride, obtained in a crystalline form by adding calcium chloride to a boiling dilute solution (0·2 per cent.) of potassium fluoride, was likewise converted into sulphate; $F = 19·02$ to 19·08.

Barium fluoride, obtained by adding potassium fluoride to a boiling solution of barium chloride, was treated in the same way; $F = 19·05—19·09$.

The action of sulphuric acid on barium fluoride is more difficult to regulate than in the first two cases, and the author regards these results as less trustworthy. Taking the mean of the results with sodium and calcium fluorides, $F = 19·05$.

C. H. B.

Solubility of Oxygen and Hydrogen in Water and in Alcohol. By W. TIMOFÉEFF (*Zeit. physikal. Chem.*, **6**, 141—152).—The author, in his investigation, employs an apparatus devised by Ostwald. It consists of an absorption-chamber which is simply a pipette provided at one end with a stopcock and at the other with a three-way tap, by means of which communication can be effected either with the air or, through a leaden capillary, with a gas burette. The pipette is filled completely with the boiled-out solvent, and a quantity of the gas to be dissolved is introduced into the gas burette and there measured. Communication is then made between the two vessels; a weighed or measured amount of water is run out through the stopcock, which is then closed, and the absorber immersed in a vessel of water at the requisite temperature. From time to time the absorber is taken out of the bath and shaken as vigorously as the flexibility of the lead tube will permit. Mercury is filled into the gas burette as required, in order that the pressure may remain as nearly that of the atmosphere as possible. When no more absorption takes place, pressure and temperature are adjusted, and a fresh measurement made.

The absorption coefficient of hydrogen in water as determined in the above way may be expressed by the formula $\beta = 0·0215286 - 0·00019216t + 0·000001722 \cdot t^2$. Bunsen found $\beta = 0·01930$ with no temperature coefficient. For oxygen in water, the author obtains $\beta = 0·041408$ at 6·4°, and $\beta = 0·036011$ at 12·6°, numbers which agree well with Winkler's results. The values for hydrogen in alcohol are fairly concordant with those of Carius, β at 0° being 0·0676 (mean of two experiments). An interpolation formula for the absorption coefficient of oxygen in alcohol of 99·7 per cent. strength is $\beta = 0·2337 - 0·00074583t + 0·000003288t^2$. The solubility of nitrogen, oxygen, carbon monoxide, and methane in water increases about 30 per cent. between 0° and 20°; the increase in alcohol is much less.

J. W.

Hydrogen Nitride (Azoimide). By T. Curtius (*Ber.*, **23**, 3023—3033). See p. 56.

Catalytic Decomposition of Ammonium Nitrite. By O. Loew (*Ber.*, **23**, 3018—3019).—On adding platinum black, prepared in the manner described in a previous paper (Abstr., 1890, 453), to a 4 to 5 per cent. solution of ammonium nitrite, an immediate evolution of gas takes place. The first portion consists of a mixture of nitrogen and nitrous oxide, but after a time nitrogen is the sole product. No noticeable alteration in the temperature of the solution occurs.

J. B. T.

Absorption of Carbonic Oxide by Earth. By Berthelot (*Compt. rend.*, **111**, 469—471).—The volume of carbonic oxide retained by air-dried clay soil is equal to the volume of air which it can retain, and hence the retention of carbonic oxide by the earth, after an explosion in a mine, for example, is not due to any specific action between the soil and the gas.

C. H. B.

Double Chloride and Dithionate of Barium. By A. Fock and K. Klüss (*Ber.*, **23**, 3001—3003).—When equivalent quantities of barium dithionate, $BaS_2O_6 + 2H_2O$, and barium chloride, $BaCl_2 + 2H_2O$, are mixed in aqueous solution, and the latter allowed to evaporate, barium dithionate first separates, then, after a time, the double salt, $BaS_2O_6,BaCl_2 + 4H_2O$, and finally barium chloride. The above double salt forms short, colourless prisms, which have been obtained 7 mm. in length and 3·5 mm. in thickness, and belong to the asymmetric system ($a : b : c = 0·6720 : 1 : 0·6398$; $\alpha = 107° 12'$, $\beta = 98° 11'$, $\gamma = 90° 57' 30''$).

H. G. C.

Action of Hydrogen on Potassium Thallium Sulphide. By R. Schneider (*J. pr. Chem.* [2], **42**, 305—327).—When the author first published his work on thio-salts (*Ann. Phys. Chem.*, **136**, **138**, **139**), he showed that when potassium thallium sulphide is heated in hydrogen it is decomposed with formation of hydrogen sulphide, potassium sulphide, and thallium sulphide. Krüss and Solereder (Abstr., 1887, 111), on the contrary, assert that the thallium is reduced to the metallic state, the potassium remaining as sulphide.

The author has reinvestigated the subject, and his experiments show that the decomposition takes place in two stages, according to the temperature; at a dark-red heat, it is in accordance with the equation which the author first gave, namely:—

$$K_2S,Tl_2S_3 + 4H = 2H_2S + K_2S + Tl_2S;$$

at a prolonged, full, red heat, however, a part of the thallium is reduced to the metallic state according to the equation

$$2[K_2S,Tl_2S_3] + 10H = 5H_2S + 2K_2S + Tl_2S + Tl_2;$$

but at no temperature at which the author has been able to obtain quantitative results is the whole of the thallium so reduced.

Krüss and Schmidt also assert (*loc. cit.*) that the salt of a thio-acid can be reduced by hydrogen when the thio-acid itself can be so reduced. But this is not the case with sodium thioantimonate or Schlippe's salt and potassium indium sulphide, which cannot be reduced by hydrogen notwithstanding that both antimony and indium sulphides are easily reduced. Compare also the behaviour of potassium platinothioplatinate, K_4PtS_4, and potassium palladothiopalladate, K_4PdS_4 (this Journal, 1871, 317).

The specific gravity of potassium thallium sulphide has been redetermined; it now stands at 4·60. A. G. B.

Researches on the Gadolinium of Marignac. By L. DE BOISBAUDRAN (*Compt. rend.*, **111**, 393—395).—Marignac's gadolinia (Abstr., 1889, 456) was fractionated with dilute ammonia. The absorption spectra showed that there was a concentration of samarium in the head fractions and of didymium in the tail. On the other hand, the fluorescence Z_β is much stronger in the head fractions, whilst the samarium fluorescence is feeble in these fractions, and is not visible in the others. The spark spectrum shows that all the fractions contain gadolinium.

Cleve finds that the greater part of gadolinia cannot be split up by fractionation. The impurities, which are difficult to eliminate, distribute themselves unequally in the different fractions, without, however, materially affecting the equivalent of the oxide.

The author observed a remarkable temporary solubility of the oxides of the rare earths in ammonium acetate solution containing excess of ammonia. A solution of gadolinium chloride, equivalent to 0·5 gram of the oxide per litre, when mixed with acetic acid and afterwards with ammonia in excess, remained transparent for a long time, but gradually became turbid, and precipitation was practically complete after a day or two. Heat accelerates precipitation, but makes it incomplete. Analogous phenomena are observed with lanthanum, yttrium, and didymium, especially the first, and in a lower degree with cerous chloride. C. H. B.

Equivalent of Terbia. By L. DE BOISBAUDRAN (*Compt. rend.*, **111**, 474—475).—In previous determinations of the equivalent of the earth Z_β (terbia with a very deep-brown colour), the quantity of oxygen existing in the earth in the form of peroxide, was uncertain. The author has repeated the determinations by the same method, that is, weighing the quantity of the sulphate formed by a given quantity of oxide, but the oxide was previously calcined at a white heat, and the small quantity of peroxide present was determined. The colour of the calcined oxide was much paler, although still very yellow; it contained 0·16 per cent. of oxygen as peroxide. The mean equivalent of the terbia is 122·32, which gives 159·48 for the atomic weight of the metal. C. H. B.

Ammonium Fluoroxymolybdates. By F. MAURO (*Gazzetta*, **20**, 109—121).—*Hexagonal ammonium fluoroxymolybdate*, $3MoO_2F_2,5NH_4F + H_2O$, prepared by dissolving the laminar fluoroxymolybdate (Abstr., 1889, 106), or the compound $MoO_3,2NH_4F$, in hydrofluoric acid, crystallises in minute, hexagonal prisms, which resemble those of the double salts of molybdenum and niobium of the type $3MoOF_3,5NH_4F + H_2O$, and are probably isomorphous with the crystals of hexagonal ammonium fluoroxyhypomolybdate. The crystals are colourless and transparent at first, but become opaque after prolonged exposure to the air; they are not dehydrated by heating at 100°; they dissolve in water, forming an acid solution, which loses hydrogen fluoride on heating, and if the temperature exceeds 100°, ammonia is also evolved.

Monammonium fluoroxymolybdate, MoO_2F_2,NH_4F, is obtained in monoclinic crystals on allowing a solution of the preceding compound in hydrofluoric acid to evaporate over sulphuric acid;

$$a : b : c = 0{\cdot}63019 : 1 : 1{\cdot}42549,\ \beta = 85° 53'.$$

Faces observed: 010, 001, 110, 111, 337, $33\bar{7}$, $66\bar{7}$. Plane of twinning (307). The crystals, which are generally twinned, are colourless and transparent, but darken and turn green after a short exposure to the air; they dissolve in water, yielding an acid solution. The crystals may be heated to 120° without losing weight, but decompose at a higher temperature.

Delafontaine's acid fluoromolybdate of ammonium appears to be identical with the author's triammonium fluoroxymolybdate, $MoO_2F_2,3NH_4F$, and is not isomorphous with the acid fluoroxytungstate.
S. B. A. A.

Double Salts of Tungstic and Vanadic Acids. By F. ROTHENBACH (*Ber.*, **23**, 3050—3060).—On adding sodium paratungstate to hydrated vanadic anhydride, sodium paratungsto-vanadate is formed, together with a compound which crystallises in dark-red octahedra, and has the formula $3(Na_2O,4WO_3),Na_2O,3V_2O_5 + 38H_2O$.

The following salts were prepared from sodium paratungstovanadate by double decomposition:—

The *ammonium salt* crystallises in orange-red octahedra of the formula $5[5(NH_4)_2O,12WO_3],2[7V_2O_5,3(NH_4)_2O] + 58H_2O$. The *barium salt* is deposited in light, orange-coloured crystals, which are very sparingly soluble, and have the formula

$$3(5BaO,12WO_3),2(5V_2O_5,2BaO) + 94H_2O.$$

From the mother liquors cubical crystals are obtained, which contain sodium chloride, barium tungstate, and barium vanadate. The *strontium salt* crystallises in orange-red cubes,

$$3(5SrO,12WO_3),2(5V_2O_5,2SrO) + 122H_2O,$$

and resembles the barium compound. The *potassium salt* crystallises in aggregates of large, light orange-red plates, which have not yet been analysed. By the action of magnesium sulphate on sodium paratungstovanadate, a compound of the formula

$$5Na_2O,12WO_3,3V_2O_5,MgO,Na_2O + 42H_2O$$

is formed, crystallising in pale orange-yellow prisms. A similar compound is deposited from the mother liquors in lustrous, light orange-coloured plates. With sodium tungstovanadate, aluminium sulphate gives a compound of the formula

$$3(Al_2O_3,9Na_2O,48WO_3),4(9V_2O_5,Al_2O_5) + 504H_2O,$$

crystallising in dark garnet-red cubes. No copper salt could be obtained.

The water of crystallisation in the above compounds was determined by cautious ignition. The vanadic acid and tungstic acid were precipitated together by means of mercuric nitrate and mercuric oxide. The vanadic acid was determined separately by reduction and titration with potassium permanganate, and also by boiling with phosphoric acid, potassium bromide, and hydrochloric acid; the bromine which is evolved is absorbed in potassium iodide solution, and the liberated iodine estimated in the usual manner.

J. B. T.

Bismuth Oxyiodide. By C. ASTRE (*J. Pharm.* [5], **22**, 195—200).—Various published methods for the preparation of this oxyiodide yielded products more or less contaminated with sub-nitrate, with oxide, or with both these compounds. To obtain the pure product, 10 grams of bismuth potassium iodide is decomposed by the addition of 4 litres of water, and the product is washed until iodine is no longer removed. The resulting compound contained Bi, 59·38, and I, 36·30 per cent. The double iodide employed is best obtained by triturating normal bismuth nitrate (1 mol.) with potassium iodide (4 mols.), and 50 c.c. of water (*sic*), extracting with ethyl acetate, and submitting the mixture to spontaneous evaporation. J. T.

Platinum Thiocarbide. By P. SCHUTZENBERGER (*Compt. rend.*, **111**, 391—393).—A current of nitrogen or hydrogen charged with the vapour of carbon bisulphide is passed over spongy platinum heated at 400—450°, and when the absorption of the bisulphide ceases, the somewhat finely divided black product is allowed to cool, and is powdered and submitted to the same treatment again. The product is a dense, black powder of the composition Pt_2CS_2. Under a microscope, it seems homogeneous, and it cannot be separated into different components by levigation. It is not attacked by boiling concentrated nitric or hydrochloric acid, and is almost entirely unaffected by warm aqua regia. It is, therefore, not a mixture of platinum sulphide with carbon, and it probably has the constitution $S\!:\!Pt\!:\!C\!:\!Pt\!:\!S$. When heated below redness in dry oxygen, it burns with incandescence, and yields carbonic anhydride, sulphuric anhydride, sulphurous anhydride, and a residue of pure platinum.

The formation of this compound may be used for the separation, and even the estimation, of carbon bisulphide in any mixture of gases which is free from oxygen. The gaseous mixture is passed over the heated spongy platinum, and the product is afterwards heated in oxygen, the gases formed being absorbed in some oxidising liquid, and the sulphuric acid estimated in the usual way. C. H. B.

Mineralogical Chemistry.

Bismuth Minerals from Gladhammar. By G. Lindström (*Jahrb. f. Min.*, 1890, ii, Ref. 53; from *Geöl. Fören. Förhandl.*, **11**, 171).—On examining a series of ores, the author found a lead-grey to tin-white mineral with a brilliant lustre. On analysis, it gave the following results:—

Bi.	Pb.	Ca.	Fe.	Zn.	S.	Insol.	Total.
33·84	48·05	0·69	0·16	0·05	15·92	0·45	99·16

The formula deduced from these results is $3PbS + Bi_2S_3$. The author is unacquainted with a mineral of this composition (compare, however, lillianite, $3Pb(Ag)S + Bi_2S_3$).

As an assay of another specimen gave 42·15 per cent. of lead, it is possible that bjelkite also occurs at Gladhammar. B. H. B.

Hamlinite, a New Rhombohedral Mineral. By W. E. Hidden and S. L. Penfield (*Amer. J. Sci.*, **39**, 511—513).—Shortly after the discovery of herderite (Abstr., 1884, 827, 1102) at Stoneham, Maine, this mineral was detected occurring as minute, rhombohedral crystals, associated with herderite, margarodite, and the rare glucinum silicate, bertrandite. During the past five years, the authors have kept up a diligent search for the crystals, but without success. The crystals are hexagonal-rhombohedral, and vary from 1 to 2 mm. in diameter. Their hardness is 4·5, and their sp. gr. 3·228. Qualitative analysis indicates that the mineral is a new species—a phosphate, probably of glucinum and aluminium, containing fluorine. The authors propose for it the name of *hamlinite*, in honour of Dr. A. C. Hamlin, who is largely interested in the development of the mineral resources of the district in which the new mineral occurs. B. H. B.

Preparation of Artificial Molybdenite. By A. v. Schulten (*Jahrb. f. Min.*, 1890, ii, Ref. 223; from *Geol. Fören. Förhandl.*, **11**, 401).—The author melted 4 grams of potassium carbonate with 6 grams of sulphur in a porcelain crucible, and on cooling added 1 gram of molybdic anhydride. The mass was then heated in a well-closed crucible to a melting heat, and, on cooling, a fresh portion of the anhydride was added. The process was repeated until 5 to 6 grams of molybdic anhydride had been used. On boiling the melted mass with water, a residue of pure crystallised molybdenite, MoS_2, was obtained in the form of greyish-violet, opaque, hexagonal crystals with a sp. gr. of 5·06 at 15°. The crystals are very soft, and make grey marks on paper. B. H. B.

Flinkite and Heliophyllite from Harstigen Mine, Sweden. By A. Hamberg (*Jahrb. f. Min.*, 1890, ii., Ref. 224—228, from *Geol. Fören. Förhandl.*, **11**, 212).—Flinkite, a hydrated manganese arsenate, occurs in the Harstigen mine, Pajsberg, Wermland, in greenish-brown crystals with sarkinite on karyopilite. Its sp. gr. is

3·87. It has a hardness of more than 4, and crystallises in the rhombic system, the forms observed being $0P, \bar{P}\infty, P, \infty\breve{P}\infty$. On analysis, it gave results corresponding with the formula

$$4H_2O,4MnO,Mn_2O_3,As_2O_5,$$

a composition very similar to that of synadelphite.

An optical examination of the mineral heliophyllite, described by G. Flink as biaxial, showed it to be always composed of biaxial and uniaxial portions. The author distinguishes two types of this mineral as met with at the Harstigen mine: (1) the coarsely laminated variety; and (2) crystals associated with barytes and inesite. The optical properties exhibited are similar to those shown by the mineral ekdemite from Långban, described by Nordenskiöld as optically uniaxial. Further, the minerals appear to be chemically identical, analysis having given the following results:—

	PbO.	FeO + MnO.	CaO.	As_2O_3.	Sb_2O_3.	Cl.
I......	83·45	—	—	10·60	—	8·00
II......	81·03	0·07	0·08	10·85	0·56	8·05
III......	80·99	0·16	0·11	10·49	1·38	7·96

I. Ekdemite (Nordenskiöld). II. Heliophyllite, type I. III the same, type II. Nordenskiöld calculates the formula, $Pb_5As_2O_8 + 2PbCl_2$, Flink gives $Pb_4As_2O_7 + 2PbCl_2$. The author, however, is of opinion that the more exact formula $Pb_9As_4O_{15} + 4PbCl_2$ is not improbable. B. H. B.

Minerals from Styria. By E. Hatle and H. Tauss (*Jahrb. f. Min.*, 1890, ii., Ref. 17; from *Verhandl. geol. Reichsanst.*, 1887, 226—229).—1. *Pharmacolite* from Völlig. This mineral occurs in white, translucent groups of crystals and crusts with a fibrous texture. Analysis yielded the following results:—

As_2O_5.	CaO.	H_2O.
48·60	27·04	24·49

The mineral is associated with zinc-blende, galena, arsenical pyrites, magnetic pyrites, iron pyrites, quartz, and calcite.

2. Iron-gymnite from Kraubath. This mineral occurs, with yellow gymnite, in serpentine. It has a hardness of 3, and a sp. gr. of 1·986. Analysis yielded the following results:—

SiO_2.	MgO.	FeO.	H_2O.
41·55	30·24	6·60	20·10

Allowance being made for 1·27 per cent. of ferric oxide disseminated in the form of iron mica, the formula is $H_{20}Mg_{12}FeS_{11}O_{45} + 9H_2O$. B. H. B.

Fluorine and the Synthesis of Minerals. By S. Meunier (*Compt. rend.*, **111**, 509—511).—The use of aluminium fluoride makes it possible to obtain in a comparatively short time, and at the temperature of an ordinary coke fire, several minerals, which under ordinary conditions are difficult to synthesise.

32 parts of calcined silica, 8 parts of fused potassium hydroxide, and 44 parts of aluminium fluoride, yield a regulus which is not completely vitreous but gives a fracture with a silky lustre. Under the microscope, it is seen to contain needles of sillimanite and hexagonal lamellæ of tridymite in large quantity, together with inclusions of various kinds and globuliform masses which are almost opaque.

43 parts of silica, 20 of calcium oxide, and 60 of aluminium fluoride yield a product which, although chiefly a glass, has a highly lustrous fracture, and contains needles of sillimanite and lamellæ of tridymite.

26 parts of silica, 12 of calcium oxide, 2 of potassium hydroxide, and 25 of aluminium fluoride yield a decidedly crystalline product containing large quantities of thin plates of labradorite, many of which are macled according to the albite law, whilst the larger have spheroidal inclusions.

22 parts of silica, 17 of alumina, 0·2 of ferric oxide, 8 of sodium hydroxide, 2 of potassium hydroxide, and 1 of lime, in a crucible brasqued with cryolite, yield a deep grey granulo-crystalline product. The mass is vitreous, but is full of inclusions, and contains many crystals of sillimanite, and a large quantity of prismatic crystals of nepheline.

27 parts of silica, 12 of alumina, and 10 of potassium hydroxide in a crucible brasqued with cryolite, yield a partially vitreous product full of crystalline granules. Under the microscope, large numbers of small globules are seen, identical with the leucite of natural amphigenes. C. H. B.

Sigterite, a New Felspar. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1890, ii, Mem. 71—74).—In an investigation into the properties of eudialyte from Sigterö, the author found that this mineral was associated with two others, white albite and another felspar in the form of grey, granular particles. The new felspar has the cleavage of orthoclase, and, chemically, is a potassium sodium felspar free from lime, and much more basic than albite and orthoclase. In thin sections, inclusions of augite and a small quantity of magnesia-mica were observed. After making corrections for the small quantities of augite present, the mineral gives on analysis the following results:—

SiO_2.	Al_2O_3.	Na_2O.	K_2O.	Total.
50·01	30·86	13·90	5·23	100·00

The formula of the felspar is therefore $(NaK)_2AlSi_3O_{10}$. In other words, it is a combination of albite and an alkali anorthite. At the same time, it has the composition of an anhydrous natrolite.

B. H. B.

Minerals from Vesuvius. By E. SCACCHI (*Zeit. Kryst. Min.*, **18**, 99—102; from *R. Accad. di Napoli*, 1888, **12**).—1. *Phakellite*, a new mineral. Among the Somma minerals in the museum of the University of Naples there is a substance, hitherto undescribed, which the author has named from its characteristic combination of transparent, colourless needles to white, silky bundles (φάκελλος). This rare mineral occurs in a rock consisting of augite with more or less mica, and occasionally in grey, granular calcite. Optically the mineral is uniaxial, with faint negative birefraction, and therefore belongs to the hexagonal system. It has the hardness of orthoclase, and a sp. gr. of 2·49. Analysis gave the following results:—

SiO_2.	Al_2O_3.	K_2O.	Na_2O.	Total.
37·73	33·33	29·30	0·37	100·73

Formula: $K_2Al_2Si_2O_8$. The analogy with nepheline is remarkable.

2. *Thermonatrite*, from the lava of 1859. This mineral is new for Vesuvius. The Naples museum recently received numerous white, opaque, drusy incrustations from the Fosso grande. On analysis, this mineral, $Na_2CO_3 + H_2O$, yielded 35·44 per cent. of carbonic anhydride.

3. *Soda* from the interior of the same lava in crystalline, colourless, transparent grains. On analysis, the following results were obtained:—

CO_2.	Na_2O.	K_2O.	H_2O.	Total.
15·91	22·15	0·41	61·68	100·15

These results correspond with the formula $Na_2CO_3 + 10H_2O$. The mineral cannot have been produced by sublimation, but by the action of carbonic anhydride which has decomposed the lava and taken the soda from it.

4. Altered *comptonite* from the Somma conglomerates. In one variety of conglomerate at Vesuvius, zeolites occur in association with calcite. Among these, small crystals resembling comptonite are occasionally met with, the change in the chemical composition of the zeolites and the variation from that of comptonite consisting chiefly in a loss of water, an absorption of calcium carbonate, and a change in the ratio of the silica to the alumina (compare Abstr., 1887, 17).

B. H. B.

Amphibolite from Habendorf, in Silesia. By E. Dathe (*Jahrb. f. Min.*, 1890, ii, Ref., 243—244; from *Jahrb. preuss. geol. Landesanst.*, 1889, 309—328).—The amphibolite (Analysis I) occurring in the biotite gneiss of Habendorf, consists of hornblende of a greenish-black colour and brilliant lustre. There is a second variety (Analysis II) composed of light greenish-grey hornblende, with a little pyrrhotite and mica. Under the microscope, olivine, diopside, chromite, and rutile could also be detected.

	SiO_2.	TiO_2.	Fe_2O_3.	Cr_2O_3.	Al_2O_3.	FeO.	MgO.	CaO.
I ..	46·47	0·21	4·18	trace	8·68	3·73	22·79	9·05
II ..	47·82	0·65	0·94	0·63	7·88	3·50	29·36	3·66

	K_2O.	Na_2O.	H_2O.	CO_2.	Total.	Sp. gr.
I ..	0·35	1·14	3·39	—	99·99	2·959
II ..	trace	0·43	4·20	0·41	99·48	2·857

B. H. B.

Chemical Nature of Tourmaline. By C. RAMMELSBERG (*Jahrb. f. Min.*, 1890, ii, Mem., 149—162).—In this paper the author recalculates some 70 analyses of tourmaline, with a view to controvert the formulæ recently arrived at by Riggs (Abstr., 1888, 660), Jannasch and Calb (Abstr., 1889, 472), Scharizer (Abstr., 1889, 764), and Wülfing (Abstr., 1889, 765). He is still of opinion that his interpretation of the tourmaline analyses of 20 years ago was correct, according to which they must be regarded as isomorphous mixtures of three silicates, R'_6SiO_5, R''_3SiO_5, and $R^{vi}SiO_5$, in which R′ represents H, Na, K, Li; R″ represents Fe, Mn, Mg, Ca; and R^{vi} represents Al_2, Fe_2, B_2, Cr_2. B. H. B.

Composition of Tourmaline. By G. W. KALB (*Jahrb. f. Min.*, 1890, ii. Ref. 199—203; from *Inaug. Diss. Göttingen*, 1890).—Ten varieties of tourmaline analysed by the author may be divided into three groups:—(1) Lithium tourmaline, (2) iron magnesium tourmaline, (3) iron tourmaline. From the analyses, the author deduces the general formula $R_9BO_2(SiO_4)_2$. [The analyses given appear to be almost identical with those given in a paper by P. Jannasch and G. Calb (Abstr., 1889, 472).] B. H. B.

Peridotite from the Harz. By M. KOCH (*Jahrb. f. Min.*, 1890, ii, Ref. 244—245; from *Zeit. deutsch. geol. Ges.*, **41**, 163—165).—Peridotite occurring in the gabbro mass of the Kaltenthal, in the Harz, contains olivine in angular grains, as much as 2½ mm. in size, with biotite, spinel, and titaniferous iron ore. Small quantities of augite and plagioclase are present as accessory constituents. The rock is more basic than any of the basic members of the Harzburg gabbro hitherto examined, as is shown by the following analytical results, in which the high percentage of titanium is probably due to the biotite:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.
34·98	5·18	10·80	1·42	21·33	19·30	0·43	5·42

Na_2O.	H_2O.	SO_3.	Total.	Sp. gr.
0·17	1·28	trace	100·31	3·27

B. H. B.

Minerals of the Garnet Group. By W. C. BRÖGGER and H. BÄCKSTRÖM (*Zeit. Kryst. Min.*, **18**, 209—276).—Of the 12 silicates crystallising in the regular system, eulytine, zunyite, helvine, danalite, garnet, sodalite, nosean, lapis-lazuli, leucite (maskelynite), pollux, analcime, and faujasite, the first eight are orthosilicates, and the last four metasilicates. Three of the metasilicates, maskelynite, pollux, and analcime, belong to one morphological group, whilst faujasite is an isolated species of octahedral type. The orthosilicates are regarded by the author as forming one large group, the garnet group, which may be subdivided into two divisions:—(1) Orthosilicates of tetrahedral character, and (2) orthosilicates of rhombic dodecahedral character. This second division includes holohedral members (the garnet series proper), as well as hemihedral ones (the alkali garnets).

The formulæ of the members of the first division are as follows:—

Eulytine......	$Bi_4(SiO_4)_3$.
Zunyite	$[Al_6F_2Cl(OH)_9]Al_2(SiO_4)_3$.
Danalite......	$(FeZnMn)_2[(ZnFe)_2S]Be_3(SiO_4)_3$.
Helvine	$(MnFeCa)_2(Mn_2S)Be_3(SiO_4)_3$.

In this voluminous paper, the author brings forward a mass of facts to prove the close connection of the regular orthosilicates. The analyses of all the minerals of this garnet group lead to formulæ in which there is 1 mol. of an orthosilicate with 3 mols. of silicic acid. All the members of this group, too, belong to the regular system. A very large number of analyses are discussed. Of these, the following have not previously been published:—

	SiO_2.	Al_2O.	CaO.	MgO.	Na_2O.	K_2O.	SO_3.	S.	Cl.	H_2O.
I.	36·74	31·96	0·11	—	25·95	trace	0·11	—	7·11	0·17
II.	37·14	31·60	—	—	25·60	—	—	—	7·31	—
III.	31·65	27·03	—	—	27·26	—	14·06	—	—	—
IV.	31·99	27·32	9·94	—	16·53	—	14·22	—	—	—
V.	32·30	27·38	8·21	0·11	18·03	0·35	12·62	0·44	0·31	—
VI.	32·20	27·37	8·18	0·11	17·98	0·35	13·17	0·46	0·33	—
VII.	32·52	27·61	6·47	—	19·45	0·28	10·46	2·71	0·47	—
VIII.	32·48	27·62	6·60	—	19·84	0·29	10·47	2·71	0·47	0·07
IX.	53·13	1·76	24·71	16·95	2·62	—	—	—	—	1·31
X.	55·15	—	26·38	18·47	—	—	—	—	—	—
XI.	55·55	—	25·93	18·52	—	—	—	—	—	—

I. Sodalite. II. Results calculated from the formula

$$Na_4(AlCl)Al_2(SiO_4)_3.$$

III. Nosean, formula $Na_4(Al[SO_4Na])Al_2(SiO_4)_3$. IV. Hauyn, formula $Na_2Ca[Al(SO_4Na)]Al_2(SiO_4)_3$. V. Hauyn, analysis. VI. Results calculated from 92 mols. hauyn, 5·2 mols. sodalite, and 2·7 mols. ultramarine with the formula $Na_4[Al(S_3Na)]Al_2(SiO_4)_3$. VII. Lapis-lazuli. VIII. The same, results calculated from a composition of 76·9 mols. hauyn, 15·7 mols. ultramarine, and 7·4 mols. sodalite. IX. Diopside occurring enclosed in lapis lazuli. X. Results after subtraction of 8 per cent. lazurite. XI. Results corresponding with formula $CaMg(SiO_3)_2$.

B. H. B.

Minerals and Rocks in the Diamond Fields of South Africa. By A. KNOP (*Jahrb. f. Min.*, ii, Ref. 97—99).—The matrix of the diamonds, the so-called *blue earth*, is found on examination to behave like a serpentine which, after decomposition by acid, leaves microliths of pyroxenic character. The rock may be described as a serpentine-tuff enclosing, at Jagersfontein, the following minerals: garnet, chrome-diopside, enstatite, chromite, zircon, apatite, idocrase, rutile, mica, and diamond. These minerals are described in detail by the author, who gives analyses of the chrome-diopside and chrome-iron ore.

The author regards the Jagersfontein deposit as having been formed from a peridotite, which has been mechanically broken up and transported to a favourably situated locality, where it has become serpentinised. The relation of the diamond to the peridotite is thought to be analogous to the occurrence of the diamond in meteorites.

B. H. B.

Natural Cement from Cairo. By E. SICKENBERGER (*Jahrb. f. Min.*, 1890, ii, Ref. 275—276; from *Zeit. deutsch. geol. Ges.*, **41**, 312—318).—On the railway between Abbasiyeh and Citadelle, near Cairo, there occur stalactitic masses hitherto thought to have been geyser deposits. On examination, they are found to consist of cemented quartz sands, approximating in composition to artificial mortar. Analysis yielded the following results :—

Sand.	SiO_2.	CaO.	$Al_2O_3 + Fe_2O_3$.	CO_2.	H_2O.	MgO.	SO_3.	NaCl.
44·90	6·24	22·80	1·47	14·00	3·84	3·58	0·58	0·24

B. H. B.

Obsidian Cliff, Yellowstone National Park. By J. P. IDDINGS (*Seventh Annual Rep. U.S. Geol. Survey*, 249—295).—The author describes in detail, in a monograph of 44 pages, illustrated by 51 plates, the geological occurrence, lithological structure, petrographical and microscopical characters of Obsidian Cliff, at the northern end of Beaver Lake, in the Yellowstone National Park. Though obsidian of nearly the same chemical composition occurs in all parts of the world, the obsidian flow at Beaver Lake is especially remarkable for its unsurpassed extent and thickness. It is the only known occurrence of rhyolitic obsidian in which a distinctly columnar structure has been developed. It is entirely free from porphyritic crystals, and abounds in spherulitic structures and lithophysæ. These are undoubtedly of primary crystallisation out of a molten glass, which was gradually cooling. Since its solidification, too, no alteration, chemical or mechanical, has taken place. B. H. B.

Eruptive Rocks of the Cabo de Gata. By A. OSANN (*Jahrb. f. Min.*, 1890, ii, Ref., 268—270; from *Zeit. deutsch. geol. Ges.*, **41**, 297—311).—The author describes in detail the occurrence of eruptive rocks at the Cabo de Gata, Almeria, Spain. The predominating rocks are andesites, dacites, and liparites. Basalts are entirely absent, as also are nepheline and leucite rocks. Only one rock contains olivine. This occurs in the vicinity of Vera and is described by Calderon as limburgite. It is the youngest of the eruptive rocks of the district, and on analysis gave results approximating most closely to those obtained with olivine-bearing lamprophyres, such as the minette of the Ballon d'Alsace. In the rock, biotite only is visible to the naked eye, whilst olivine, augite, and a little felspar can be detected under the microscope. The analytical results were as follows :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	K_2O.	Na_2O.
55·17	13·49	3·10	3·55	0·39	8·55	3·15	1·09	4·43

H_2O.	CO_2.	Total.
4·27	3·27	100·46

The rock is named *Verite* by the author. It should certainly not be classed as a limburgite. B. H. B.

Meteoric Iron from Magura, Arva, Hungary. By E. WEINSCHENK (*Jahrb. f. Min.*, 1890, ii, Ref. 57—59; from *Ann. k. k. Hofmuseums*, **4**, 93—101; compare Berthelot and Friedel, Abstr., 1890, 1384).—In an investigation of the meteoric iron from Magura, Arva county, Hungary, the author succeeded in isolating the following constituents:—

1. Tin-white regular crystals, hitherto regarded as schreibersite. These appear to have a cleavage perpendicular to the longitudinal axis; they are strongly magnetic, very brittle, and soluble in hydrochloric acid and copper ammonium chloride, with separation of carbon. The hardness is 5½ to 6, and the sp. gr. 6·977. Analysis (No. I) gave, after subtraction of schreibersite, results corresponding with the formula $C(FeNiCo)_3$. For this new mineral, the author proposes the name of *cohenite*.

2. Thin, silver-white, strongly magnetic lamellæ, which are but slowly soluble in hydrochloric acid, and which may represent Reichenbach's *tænite*. The composition (Analysis II) is in accord with the formula $Fe_5(NiCo)_2$.

3. Fragments of various shapes, which form the principal mass of the iron. They are highly magnetic, sparingly soluble in hydrochloric acid, and give on analysis (No. III) results corresponding with the formula $Fe_8(NiCo)$. The high percentage of cobalt is noteworthy—

	Fe.	Ni.	Co.	C.	Cu.	Sn.	Schreibersite.	Total.
I.	89·83	3·08	0·79	6·43	trace	trace	0·65	100·78
II.	71·04	26·64	1·67	0·30	—	—	—	99·65
III.	87·96	9·19	2·60	0·36	—	—	—	100·11

4. Crystals of rhombic and monoclinic augite.

5. Grains of partly isotropic, partly feebly bi-refractive, diamond proved to be harder than ruby and to burn to carbonic anhydride in a current of oxygen.

Colourless or strongly pleochroic blue grains appear to consist of corundum, whilst small, colourless aggregates may be tridymite.

The author compares the varieties of carbon met with in meteoric iron with those in pig iron. The "hardening-carbon" corresponds with the carbon given off in the form of hydrocarbons when the meteoric iron is dissolved in hydrochloric acid; the ordinary carbide carbon corresponds with cohenite; the graphitic tempering-carbon with the carbon in the residue when meteoric iron is dissolved; and, lastly, graphite is met with in both varieties of iron. This perfect analogy leads to the assumption that the conditions under which meteoric iron was formed are comparable to those under which pig iron is produced, and the presence of the diamond indicates that the carbon dissolved or chemically combined in iron can under certain conditions separate out in the allotropic form of the diamond.

B. H. B.

Organic Chemistry.

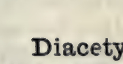
Condensation of Acetylene by the Silent Discharge. By Berthelot (*Compt. rend.*, **111**, 471—472.)—If the product of the condensation of acetylene under the influence of the silent discharge is left exposed to the air, it absorbs about one quarter of its weight of oxygen, and can easily be detached from the glass in the form of a yellow, resinous pellicle. It continues to alter spontaneously in the vessel in which it is placed, with formation of a carbonaceous sublimate which is probably the result of a secondary change. When subjected to dry distillation, it undergoes sudden and explosive decomposition, which seems to be exothermic, with production of a considerable quantity of water, together with some acetic acid, and acetonic liquids which have an odour of caramel, and are similar to, if not identical with, the products from sugar or tartaric acid. Neither benzene nor furfuraldehyde is obtained, and distillation with soda-lime yields acetone and other simple products. It is clear therefore that the condensation of acetylene under the influence of the silent discharge is very different from its condensation under the influence of heat. C. H. B.

Combination of Mercuric Cyanide with Lithium Salts. By R. Varet (*Compt. rend.*, **111**, 526—527).—A concentrated solution of lithium iodide is added drop by drop to a saturated solution of mercuric cyanide heated at 50—60°. A further quantity of mercuric cyanide is then dissolved in the liquid and more lithium iodide is added. The liquid is concentrated to a syrup, filtered, and allowed to cool, when it deposits the compound $HgCy_2,2LiCy,HgI_2 + 7H_2O$ in large nacreous lamellæ, which are hygroscopic, very soluble in water, and lose 3 mols. H_2O at 100°, but cannot be completely dehydrated without decomposing. When the salt is carefully heated, it gives off water and becomes yellow, a sublimate of mercuric iodide forming at the same time. At a higher temperature, the salt melts and decomposes into mercuric iodide, mercury, cyanogen, and mercurous iodide. Dilute acids decompose the salt with liberation of hydrocyanic acid and precipitation of mercuric iodide, whilst mercuric cyanide and a lithium salt of the particular acid remain in solution. Copper sulphate, when heated with a solution of the salt, precipitates cuprous cyanide and mercuric iodide, a result which indicates that all the cyanogen is not combined with the mercury. These reactions show that the constitution of the compound is expressed by the formulæ given.

If lithium bromide is added gradually and in small quantity to a saturated solution of mercuric cyanide heated at 80°, the liquid, on cooling, deposits crystals of the compound $HgCy_2,LiBr + 3\frac{1}{2}H_2O$. They are hygroscopic and very soluble in water, lose $1\frac{1}{2}$ mols. H_2O at 100°, but cannot be dehydrated without decomposing. When heated gently, it yields no sublimate of mercuric bromide, but at a high temperature it undergoes complex decomposition. When heated with copper sulphate solution, no cyanogen is evolved, and no precipitate is formed; it follows that all the cyanogen is combined with the mercury.

A mercury lithium cyanochloride is obtained by evaporating a solution of mercuric cyanide containing an excess of lithium chloride. It is so hygroscopic that its composition could not be ascertained.

C. H. B.

Ethylene Dithiocyanate. By C. PARENTI (*Gazzetta*, **20**, 178—183).—By treating perthiocyanic acid with alcoholic potash, Fleischer (this Journal, 1871, 391) obtained a compound isomeric with potassium thio- and isothio-cyanate, but differing from these compounds in several respects (*Annalen*, **179**, 204). The acid formed by decomposing this salt with sulphuric acid was considered to be a dithiocyanic acid. To prepare the ethylene derivative, perthiocyanic acid and ethylene bromide in molecular proportion are dissolved in the least possible quantity of alcohol, mixed with an alcoholic solution of potassium hydroxide, and boiled for 5 to 6 hours. The filtered liquid, on cooling, deposits a semi-crystalline mass, part of which is insoluble in boiling water, and remains in hard ill-defined crystals which melt at 137—140°. The soluble portion, on recrystallisation from boiling water, is obtained in slightly yellowish prisms which melt at 149—150°, and are readily soluble in hot water and alcohol, but insoluble in ether and benzene. It dissolves in cold concentrated sulphuric acid, and is reprecipitated unaltered on the addition of water. After fusion, it resolidifies at 130°, but this temperature is reduced to 118° after successive fusions. The aqueous solution is not coloured by ferric chloride even after acidification with hydrochloric acid; on heating the alkaline solutions, the respective thiocyanates are formed. The constitution of this salt is probably  $\overset{\diagup CS \diagdown}{\underset{\diagdown CS \diagup}{N\cdot C_2H_4\cdot N}}$. The compound melting at 137—140° has the composition $C_4N_4S_3(C_2H_4)_2$; it is slightly soluble in cold concentrated sulphuric acid, and, on warming, a green liquid with a blue fluorescence is produced from which sulphur separates after a time.

S. B. A. A.

Diacetylcarbinyl Acetate. By A. COMBES (*Compt. rend.*, **111**, 421—423).—Chloracetylacetone (Abstr., 1890, 1394), when boiled with potassium acetate in presence of alcohol, yields a pale-yellow liquid which boils at 74·5° under a pressure of 21 mm., also a large quantity of ethyl acetate. The new product has the composition $C_6H_8O_3$; it has an acid odour, but yields no metallic derivatives, and reduces Fehling's solution and ammoniacal silver nitrate in the cold. It yields a very unstable hydrazone $C_{11}H_{14}N_2O_2$, which resinifies rapidly when exposed to air and light, and crystallises from ether in large colourless rhomboidal tables which rapidly become red when exposed to light. If this hydrazone is treated with excess of phenylhydrazine in alcoholic solution, it yields an osazone $C_{15}H_{16}N_4$, very soluble in ether, from which it is precipitated by light petroleum in crystals melting at 143—144°. It is the osazone of acetol, and can also be obtained by the direct action of phenylhydrazine on a hot solution of the compound $C_5H_8O_3$ in acetic acid.

The compound $C_5H_8O_3$ is in fact the acetate of acetol, formed in accordance with the equations $CHAc_2Cl + AcOK = CHAc_2{\cdot}OAc + KCl$; $CHAc_2{\cdot}OAc + EtOH = CH_2Ac{\cdot}OAc + AcOEt$.

In order to avoid the secondary action of the alcohol, monochloracetylacetone was boiled for four or five hours with potassium acetate in presence of glacial acetic acid, and the product was poured into water and mixed with concentrated cupric acetate solution. A green precipitate separates, and is purified by solution in chloroform and precipitation with ether; it forms deep-green crystals of the composition $(C_7H_9O_4)_2Cu$, and is the cupric salt of diacetylcarbinol, $CHAc_2{\cdot}OAc$, which contains a basic hydrogen atom in the group $\equiv CH{\cdot}OAc$. The copper salt is dissolved in dilute sulphuric acid, and the solution is extracted with ether. After the ether has been expelled, the diacetylcarbinyl acetate is obtained as a colourless liquid boiling at 111° under a pressure of 21 mm. It reduces Fehling's solution and ammoniacal silver nitrate in the cold, has a strongly acid reaction, and decomposes carbonates with formation of crystallisable metallic derivatives. When treated with phenylhydrazine, it yields a viscous liquid which boils without decomposition in a vacuum at 235—240°, and which, when treated with hot sulphuric acid or with oxidising agents, yields a beautiful, blue colouring matter, insoluble in water, but soluble in chloroform or sulphuric acid, and having all the characteristics of a pyrazole-blue.

Attempts to obtain diacetylcarbinol by saponification of the acetate have not yet been successful. C. H. B.

Indian Geranium Oil: Oxidation of Geraniol. By F. W. Semmler (*Ber.*, **23**, 2965—2968; see also Abstr., 1890, 951).—For the oxidation of geraniol, potassium dichromate (10 grams) is dissolved in sulphuric acid (12·5 grams) and water (100 grams), and the geraniol added (15 grams all at once), the mixture being at first well cooled, and afterwards allowed to become warm, and vigorously shaken for half an hour. The whole is then made slightly alkaline and distilled in a current of steam. The distillate contains an oil, which has a pleasant odour resembling oranges and lemons, and is a mixture of the oxidation product with ethereal oils formed by the action of the sulphuric acid on geraniol. To separate the latter, the oil is mixed with a saturated solution of sodium hydrogen sulphite, and allowed to remain for 24 hours. The crystalline magma is then collected, pressed between filter-paper, washed with ether, mixed with sodium carbonate, and distilled in a current of steam. A clear, colourless oil, having the composition $C_{10}H_{16}O$ and the above-mentioned characteristic odour, is thus obtained, and appears from its general reactions to be an aldehyde. It is at present being more closely examined.

Alkaline potassium permanganate acts on geraniol in a different manner, yielding a polyvalent alcohol, which has the closest resemblance to the sugars. H. G. C.

Dihydric Alcohols derived from Isobutaldehyde. By E. SWOBODA and W. FOSSEK (*Monatsh.*, **11**, 383—398).—It has been previously shown (compare Abstr., 1884, 37, 832) that when alcoholic potash acts on a mixture of isobutaldehyde and acetaldehyde, *methylisopropylethylene glycol*, $OH \cdot CHMe \cdot CHPr^{\beta}.OH$, boiling at 206—207°, is formed. When valeraldehyde and benzaldehyde are substituted for acetaldehyde, *isobutylisopropylethylene glycol*,

$$CHMe_2 \cdot CH_2 \cdot CH(OH) \cdot CHPr^{\beta} \cdot OH,$$

which melts at 79—80° and boils at 231—232°, and *phenylisopropylethylene glycol*, $OH \cdot CHPh \cdot CHPr^{\beta} \cdot OH$, melting at 81—82° and boiling at 286—287°, are formed respectively. In the formation of isobutylisopropylethylene glycol, potassium isobutyrate is the only other product; it must therefore be supposed that a molecule of isobutaldehyde unites with a molecule of valeraldehyde through their aldehydic carbon atoms, which, at the moment of condensation, take up each an atom of hydrogen, furnished by the oxidation of another molecule of isobutaldehyde by a molecule of potassium hydroxide.

The three glycols yield diacetyl derivatives, when heated for 18 hours, in sealed tubes, at 200°, with an excess of acetic anhydride. The compounds thus obtained from methylisopropyl glycol, isopropylisobutylethylene glycol and phenylisopropylethylene glycol, have respectively the formulæ $C_{10}H_{18}O_4$, $C_{13}H_{22}O_4$, and $C_{15}H_{20}O_4$, and the boiling points 220°, 240—242°, and 295—297°.

On treatment with sulphuric acid, the three glycols behave as pinacones, and lose the elements of a molecule of water; isopropylisobutyl glycol is converted by cold concentrated sulphuric acid into an α-pinacoline, $C_9H_{18}O$, which boils at 150° and has the odour of camphor, and by hot dilute acid into a β-pinacoline, $(C_9H_{18}O)_2$, which boils at 274° and is without odour. The other glycols give similar products.

G. T. M.

Sugars derived from Rhamnose. By E. FISCHER and O. PILOTY (*Ber.*, **23**, 3102—3110).—Rhamnose (isodulcite) is methylpentose, has the formula $CH_3 \cdot [CH \cdot OH]_4 \cdot CHO$, and, like the other heptoses, yields sugars richer in carbon. It is proposed to term these derivatives rhamnohexose, rhamnoheptose, and rhamnooctose.

Rhamnitol, $CH_3 \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot OH$, is prepared by the reduction of rhamnose with sodium amalgam, and crystallises from alcohol or acetone in triclinic prisms, which melt at 121°, and are insoluble in ether. It is sweet to the taste, is only partially decomposed on distillation, and does not reduce alkaline copper solution. It is readily oxidised by nitric acid, and is reduced by hydriodic acid. The yield is 60 per cent. of the rhamnose.

Rhamnohexonic acid, $CH_3 \cdot [CH \cdot OH]_5 \cdot COOH$, is already known by the name isodulcitolcarboxylic acid, or rhamnosecarboxylic acid (comp. Abstr., 1888, 806).

Rhamnohexose, $CH_3 \cdot [CH \cdot OH]_5 \cdot CHO$, is prepared by the reduction of rhamnohexolactone with sodium amalgam at a low temperature;

the yield is 60—65 per cent. of the lactose. The compound crystallises from methyl alcohol in thick plates which melt at 180—181° with decomposition, and exhibit all the characteristic properties of sugar. It does not ferment with yeast. The *phenylhydrazone* is readily soluble in water. The *osazone* is obtained in stellate groups of yellow needles which melt at 200° with evolution of gas, and are readily soluble in alcohol, but nearly insoluble in water.

Rhamnohexitol, $CH_3\cdot[CH\cdot OH]_5\cdot CH_2.OH$, is prepared in a similar manner to rhamnitol, and crystallises from alcohol in small, colourless prisms which melt at 173°, with previous softening at 170°, and have no action on alkaline copper solution.

Rhamnoheptonic acid, $CH_3\cdot[CH\cdot OH]_6\cdot COOH$, is formed by the action of hydrogen cyanide on rhamnohexose; on evaporation, it readily passes into the lactone, which crystallises from alcohol in stellate groups of colourless needles melting at 160°, with previous softening at 158°; the yield is 63 per cent. of the sugar.

Rhamnoheptonic hydrazide, $C_8H_{15}O_7\cdot N_2H_2Ph$, is formed by the action of phenylhydrazine acetate on the acid or lactone; it crystallises from water in slender, white needles which melt above 215° with evolution of gas, and are very sparingly soluble in alcohol.

Rhamnoheptose, $CH_3\cdot[CH\cdot OH]_6\cdot CHO$, is prepared by the reduction of the lactone, and could not be obtained in crystals; it is readily soluble in water or alcohol, but insoluble in ether. The *phenylhydrazone* crystallises from water in colourless, slender needles; on treatment with hydrochloric acid, the sugar is regenerated. The *osazone* is deposited in slender, yellow needles, which are very sparingly soluble in water or alcohol, and melt at about 200° with decomposition.

Rhamnoctonic acid, $CH_3\cdot[CH\cdot OH]_7\cdot COOH$, is prepared from rhamnoheptose; on evaporation, the *lactone* is formed, and is best purified by means of the phenylhydrazone; it crystallises from water in colourless, concentric needles which melt at 171—172° without decomposition, and are readily soluble in water or alcohol, but sparingly so in acetone.

The *phenylhydrazide*, $CH_3\cdot[CH\cdot OH]_7\cdot CO\cdot N_2H_2Ph$, crystallises from water in slender, white needles melting at 220°. *Rhamnoctose* is formed in small quantity by the reduction of the lactone; it readily reacts with alkaline copper solution, and yields an *osazone*, which is insoluble in water, and melts at 216°.

The following table gives the specific rotatory powers of the rhamnose compounds, as far as they are known :—

	Specific rotation.
Rhamonolactone	—
Rhamnose	+ 8° to 9°
Rhamnitol	+10·7
Rhamnohexonolactone	+83·8
Rhamnohexose	−61·1
Rhamnohexitol (approximate)	+11·6
Rhamnoheptonolactone	+55·6
Rhamnoheptose (approximate)	+ 8·4
Rhamnoctonolactone	−51·20

J. B. T.

Arabinose from Wheat Bran and Rye Bran. By E. STEIGER and E. SCHULZE (*Ber.*, **23**, 3110—3113).—It has been previously pointed out by Tollens and his pupils that in all probability the formation of furfuraldehyde from wheat bran and from rye bran by the action of sulphuric acid depends on the previous decomposition of pentaglucoses (arabinose and xylose); neither of these compounds has, however, hitherto been isolated from the product of the reaction. Wheat bran, freed from starch and albuminous matter, is boiled for several hours with 3 per cent. dilute sulphuric acid; the acid is neutralised with barium carbonate, the solution filtered, concentrated, and extracted with alcohol; on evaporation, arabinose crystallises out; it was identified by its specific rotatory power, and its ozazone.

The arabinose is probably formed by the hydrolysis of a compound which the authors term *metaraban*. This is a constituent of the cell membrane, and cannot be prepared quite pure. It gives a cherry-red colour on warming with hydrochloric acid and phloroglucinol, and is insoluble in water, and in cold dilute alkalis or acids. On warming, it readily dissolves, and becomes converted into sugar. Other samples of wheat bran gave similar results, as did also rye bran. No galactose or mannose could be detected in any of the solutions. J. B. T.

Starch. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **23**, 3060—3075).—The authors give a historical review of the investigation of starch and of the compounds derived from it by hydrolysis, followed by a sketch of the recent work and present theories on the subject.

The experimental part of the present communication is limited to an investigation of dextrin.

Commercial dextrin can be purified by precipitation with alcohol, care being taken that the quantity of alcohol present never exceeds 85 per cent. of the total solution; after precipitating three times, the product ceases to give an insoluble osazone, and after repeating the operation several times the dextrin may be considered to be free from sugar. Good results are also obtained by dialysis and subsequent precipitation with alcohol, but a product free from sugar could not be produced by fermentation.

Pure dextrin becomes yellow or brown on heating with potash, and it readily reduces alkaline copper solution, thus showing that, as it is itself not a definite compound, its constituents must belong wholly, or in great part, to the class of sugars which contain an aldehydic or ketonic group.

This view is supported by the fact that, on digesting solid dextrin with excess of phenylhydrazine at ordinary temperatures, it dissolves, and on heating with alcohol a white precipitate is obtained; this is washed free from phenylhydrazine, and purified by dissolving in water and precipitating with alcohol. This compound contains 1·02 per cent. of nitrogen, corresponding with the formula $C_{96}H_{62}O_{80}{\cdot}N_2HPh$, and closely resembles dextrin in its chemical properties and in solubility; it is decomposed by hydrochloric acid in a manner similar to the phenylhydrazones of sugars with high molecular weights. By heating on the water-bath for two hours with phenylhydrazine acetate, and treating the product with alcohol, a pale-yellow *osazone* is formed, which is less soluble in water than the phenylhydrazone, and may be precipitated by alcohol. The percentage of nitrogen varies somewhat, thus showing that in all probability the body is a mixture of osazone with unaltered phenylhydrazone.

An aqueous solution containing 8 per cent. of dextrin is repeatedly treated with small quantities of sodium amalgam, dilute acetic acid being added from time to time; after several days, alcohol is added to the slightly acid solution, and the insoluble product purified by repeatedly dissolving in water and precipitating with alcohol. The authors propose to call this colourless compound *dextritol;* it does not reduce alkaline copper solution, is insoluble in phenylhydrazine even on warming, and the solution does not become yellow on boiling with potash. By the action of concentrated acids or of diastase on dextritol, a liquid is formed which readily reduces alkaline copper solution.

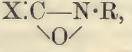
An 8 per cent. aqueous solution of dextrin is heated with a few drops of bromine and allowed to stand until the colour disappears, a second quantity of bromine is then added, and, as soon as this has reacted, the dextrin is precipitated with alcohol in order to free it from hydrobromic acid; the product is dissolved in water and treated with bromine as before, the process being repeated until the dextrin ceases to reduce alkaline copper solution. After repeated purification, a white powder is obtained which is soluble in phenylhydrazine; an aqueous solution reddens litmus paper, and decomposes calcium carbonate on warming. No precipitate is obtained with lime-water and lead acetate; by the action of diastase, or by heating with a mineral acid, a product is obtained which readily reduces alkaline copper solution.

The above results all point to the presence of an aldehydic group in dextrin, and this view is supported by the fact that the products of hydrolysis are also aldehydes.

By the hydrolysis of starch, the authors have only obtained glucose, but from commercial "starch sugar" they have isolated an unfermentable compound which resembles dextrin, and, from the analysis of its osazone, has the formula $C_{12}H_{22}O_{11}$, being thus isomeric with maltose.

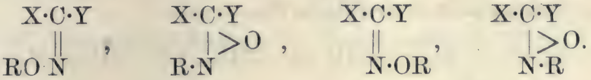
J. B. T.

Stereochemical Isomerides of Nitrogen Compounds. By A. HANTZSCH and A. WERNER (*Ber.*, **23**, 2764—2769; see also Abstr., 1890, 348, 970).—The authors in this paper sum up their views with regard to the isomeric relationships of the oximes as follows:—(1.) The oximes $X\colon C\colon N\cdot OH$ behave as tautomeric compounds, and yield two different alkyl derivatives having the structural formulæ $X\colon C\colon N\cdot OR$ and $X\colon\underset{\diagdown O\diagup}{C—N}\cdot R$, which may be distinguished as "oxygen ethers" and "nitrogen ethers." (2.) Certain asymmetrical oximes exist in two stereochemically isomeric forms, which, according to the theory proposed by the authors, are represented by the formulæ



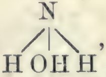
$X\colon\underset{\diagdown O\diagup}{C—N}\cdot R$

$\begin{array}{c}X\cdot C\cdot Y\\ \|\\ HO\cdot N\end{array}$ and $\begin{array}{c}X\cdot C\cdot Y\\ \|\\ N\cdot OH\end{array}$. (3.) Each of these isomerides can yield two structurally isomeric ethyl derivatives, and therefore an asymmetrical oxime of the formula $\genfrac{}{}{0pt}{}{X}{Y}{>}C\colon N\cdot OH$ should yield four alkyl derivatives, namely:—



$$\begin{array}{c}X\cdot C\cdot Y\\ \|\\ RO\cdot N\end{array},\quad \begin{array}{l}X\cdot C\cdot Y\\ \quad\;|{>}O\\ R\cdot N\end{array},\quad \begin{array}{c}X\cdot C\cdot Y\\ \|\\ N\cdot OR\end{array},\quad \begin{array}{l}X\cdot C\cdot Y\\ \quad\;|{>}O.\\ N\cdot R\end{array}$$

In no one case have all four alkyl derivatives been prepared, only three being known in most cases, two of these being "oxygen ethers" and one a "nitrogen ether." In the case of furfuraldoxime, however, the two isomeric "nitrogen ethers" have been prepared, thus giving an indirect proof of this part of the theory.

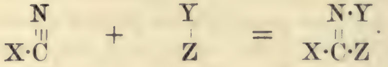
Auwers and Meyer have suggested that the isomerism of the oximes is due, not to the nitrogen atom, but to the asymmetrical constitution of the hydroxylamine itself, as represented in the formulæ $\genfrac{}{}{0pt}{}{X}{Y}{>}C\colon N\cdot O{}^{\diagup H}$ and $\genfrac{}{}{0pt}{}{X}{Y}{>}C\colon N\cdot O{}_{\diagdown H}$ (Abstr., 1890, 1264). The authors point out that this hypothesis does not explain the existence of two isomeric nitrogen ethers, and also that the formulæ proposed by Auwers and Meyer do not represent distinct isomerides, but only phases of an intermolecular atomic motion, which pass one into the other by the simple rotation of the hydrogen atom of the hydroxyl group around the axis N—O. Further, if, owing to the combined attraction of the nitrogen atom as well as that of the oxygen atom, the hydrogen atom takes up a position intermediate between the two, it must be also supposed that the oxygen atom is attracted out of the plane by the hydrogen atoms of the amido-group; this, however, simply means, in other words, that the hydroxylamine molecule assumes the tetrahedral configuration  $\begin{array}{c}N\\ \diagup|\diagdown\\ H\;OH\;H\end{array}$, which is simply a special case of the authors' general hypothesis. According to Behrend's hypothesis (Abstr., 1890, 575), the isomeric benzaldoximes should show very slight differences in their physical properties, but, as a matter of fact, the two compounds are completely distinct. Moreover, the latter hypothesis gives no explanation of the ready formation of benzonitrile from isobenzaldoxime.

In conclusion, the authors state that their hypothesis, like those of Van't Hoff and Wislicenus, is not dependent on any special assumption as to the direction of valencies, &c., but is simply deduced from general symmetrical relations. H. G. C.

Attempts to prepare Stereochemical Isomerides of Nitrogen Compounds. By A. HANTZSCH (*Ber.*, **23**, 2769—2773).—The investigation described in this paper was undertaken to determine, if possible, the conditions under which stereochemical isomerides of nitrogen compounds are formed. (1.) The study of the question of the existence of an asymmetrical nitrogen atom in derivatives of ammonia and of hydrazine has not yet led to any positive results (see also Kraft, following abstract). (2.) All attempts to obtain stereochemical isomerides of compounds, other than the oximes, with a double linkage between the nitrogen and carbon atom, have been without success. It was found that urethanes do not condense with carbonyl compounds according to the equation

$$=\mathrm{CO} + \mathrm{H_2N{\cdot}COOR} = \;=\mathrm{C{=}N{\cdot}COOR} + \mathrm{H_2O},$$

and that isomeric derivatives cannot be obtained from benzylidineaniline (this vol., p. 50). Further, it was found that nitriles do not form additive compounds in the manner represented by the equation :—



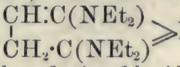
$$\begin{array}{c}\mathrm{N}\\ \vert\vert\vert\\ \mathrm{X{\cdot}C}\end{array} + \begin{array}{c}\mathrm{Y}\\ \vert\\ \mathrm{Z}\end{array} = \begin{array}{c}\mathrm{N{\cdot}Y}\\ \vert\vert\\ \mathrm{X{\cdot}C{\cdot}Z}\end{array}.$$

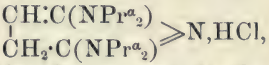
(3.) The compounds which yield isomeric oximes include almost all aromatic aldehydes and asymmetrical ketones, their meta- and para-substitution products, and also diketones of the benzile type and phenylglyoxylic acid. The fatty aldehydes and ketones, and all compounds containing even a single alcohol radicle, C_nH_{2n+1}, in combination with the carbonyl group, yield only a single oxime. This is also the case with all compounds containing a carbonyl group in a closed chain, and in all aromatic aldehydes and ketones in which substitution has taken place in the ortho-position relatively to the carbonyl group. When substitution has taken place in both ortho-positions, the compound does not yield any oxime. This agrees with the results of Kehrmann, but the author differs from Kehrmann in so far as he regards the configuration of the molecule, rather than the space which it occupies, as determining the possibility of the existence of isomerides.

H. G. C.

Displacement of Halogens by the Amido-group. By E. SEELIG (*Ber.*, **23**, 2971—2972).—In the usual process for the displacement of a halogen by the amido-group by treatment with with aqueous or alcoholic ammonia, the reaction, as a rule, does not stop with the simple displacement, but proceeds further, with formation of secondary and tertiary bases. If, in place of the solution of ammonia in water or in alcohol, phenol diluted with 15 per cent. of water and saturated with gaseous ammonia is employed, the reaction proceeds much more smoothly. Thus benzyl chloride treated with this reagent gives 24 per cent. of the theoretical yield of benzylamine, whereas with aqueous or alcoholic ammonia, only traces of the amine are obtained. Ethylene bromide, treated in a similar manner, gives a yield of 38 per cent. of ethylenediamine hydrate. H. G. C.

Isobutylamine. By H. MALBOT (*Compt. rend.*, **111**, 528—529).—The author has investigated the conditions which give the largest yield of isobutylamine by the reaction of isobutyl chloride with ammonia. The chloride was heated with different proportions of ammonia in sealed tubes at 100° for various periods of time. Details of the experiments are given. The best results are obtained when 1 mol. of isobutyl chloride is heated with 10 or 15 mols. of ammonia; in the first case the quantity of diisobutylamine formed is twice as great as in the second, but it is easily removed by washing with water. The mixture must be heated for 3 to 3½ days. C. H. B.

Action of Secondary Amines on Imido-ethers. By A. PINNER (*Ber.*, **23**, 2927—2933).—*Tetrethylsuccinamidine hydrochloride*, $NH:C(NEt_2)\cdot CH_2\cdot C(NH)\cdot NEt_2,2HCl$, is prepared by the action of diethylamine on ethylsuccinimidine hydrochloride; after remaining for about eight days, it separates in lustrous, prismatic crystals. On recrystallisation, ammonia is eliminated, and *tetrethylsuccinimidine hydrochloride*,  $\begin{matrix} CH:C(NEt_2) \\ | \\ CH_2\cdot C(NEt_2) \end{matrix} > N,HCl$, is formed, crystallising in large, thin plates. The *platinochloride* is deposited in yellowish-red, lustrous, pointed prisms which melt at 202°.

Tetrapropylsuccinimidine hydrochloride,  $\begin{matrix} CH:C(NPr^{a}_2) \\ | \\ CH_2\cdot C(NPr^{a}_2) \end{matrix} > N,HCl$, which closely resembles the tetrethyl derivative, is prepared by the action of dipropylamine on phenylsuccinimide hydrochloride; the intermediate succinamidine could not be isolated; the condensation takes place much more readily than with diethylamine. The *nitrate*, $C_{16}H_{31}N_3,2HNO_3$, melts at 53°. The *platinochloride* is very sparingly soluble in water, from which it crystallises in large, pale yellow plates melting at 174°.

The constitution of the above compounds cannot be regarded as being definitely proved, but the formulæ assigned to them appear to be the most probable. J. B. T.

β-Bromopropaldehyde and β-Bromopropionic Acid. By L. LEDERER (*J. pr. Chem.* [2], **42**, 384). *β-Bromopropaldehyde* is obtained by passing dry hydrogen bromide into well-cooled acraldehyde to saturation, and evaporating the excess of acraldehyde at a low temperature. It is a thick, yellowish oil, and does not crystallise; it soon decomposes at the ordinary temperature, and, when heated to 45° in absence of air, it evolves hydrogen bromide and chars.

β-Bromopropionic acid, obtained by oxidising the aldehyde with well-cooled nitric acid (sp. gr. 1·48) and extracting with ether, crystallises in large, colourless tables which melt at 62·5°, and dissolve in the usual solvents (Beckurts and Otto, Abstr., 1885, 506). The *ethyl salt* boils at 89° (40—50 mm.). A. G. B.

Action of Hydrocyanic Acid on Unsaturated Aldehydes. By G. JOHANNY (*Monatsh.*, **11**, 399—412; compare Gautier, *Bull. Soc. Chim.*, **25**, 481; Lobry de Bruyn, Abstr., 1885, 242; 1886, 224).—When methylethylacraldehyde is heated with an equal volume of anhydrous hydrocyanic acid in sealed tubes for 50 hours at 45°, the hydrocyanide,

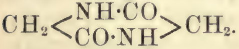
$C_6H_{10}O,HCN$, is formed, but the compound is so unstable that it cannot be isolated in a pure state, although its acetyl derivative $CHEt.CMe\cdot CH(CN)\cdot OAc$, obtained by heating it with excess of acetic anhydride in a reflux apparatus, may be distilled without decomposition at 110—114° under a reduced pressure of 38 mm.

α-Hydroxy-β-propylidinebutyramide,

$$CHEt\colon CMe\cdot CH(OH)\cdot CONH_2,$$

is formed when the above-described acetyl compound is treated with five times its weight of fuming hydrochloric acid and the mixture is allowed to remain at ordinary temperatures in a closed flask for three days. From an alcoholic solution, it crystallises in colourless, rhombic plates which melt at 100—101°, and on heating with milk of lime, ammonia is evolved, and the calcium salt of α-hydroxypropylidenebutyric acid, $(C_7H_{11}O_3)_2Ca + 2H_2O$, obtained; this crystallises from water in needles. G. T. M.

Molecular Weight of Glycocine and its Anhydride. By T. CURTIUS and H. SCHULZ (*Ber.*, **23**, 3041—3043).—Determinations of the molecular weights of amidoacetic acid and of various derivatives by Raoult's method, with water as the solvent, give results in accordance with the simple formula $NH_2\cdot CH_2\cdot COOH$. Similar experiments with the anhydride point to the formula



$$CH_2<\begin{matrix}NH\cdot CO\\CO\cdot NH\end{matrix}>CH_2.$$

The results previously obtained from vapour density determinations by Hofmann's method are thus fully confirmed. J. B. T.

Glycocine. By J. MAUTHNER and W. SUIDA (*Monatsh.*, **11**, 373—382; compare Abstr., 1889, 139).—The authors have prepared glycocine by a more satisfactory method than those previously described, in the following way:—To a well-cooled solution of chloracetic acid (100 grams) in water (100 c.c.) or alcohol, 20—22 per cent. aqueous ammonia (1 litre) was gradually added. After remaining for a week at ordinary temperatures, the solution was heated, first alone, and then with lead oxide, to expel ammonia; after filtering, the lead was precipitated by the addition of freshly prepared ammonium sulphide, the lead sulphide filtered off, the solution evaporated to dryness, and the crystalline mass thus obtained dissolved in a little water and boiled with copper carbonate. On cooling the filtered solution, copper glycocine crystallised out in masses of needles which, when recrystallised from a little water, gave, besides the needles, a number of bluish-violet, glistening scales. These scales have a similar composition, $(C_2H_4NO_2)_2Cu + H_2O$, to the needles, but give up their water of crystallisation at a much lower temperature. The modification crystallising in scales may be obtained by heating the needles with a quantity of water insufficient to completely dissolve them, rapidly filtering, and allowing the solution to crystallise. The yield of copper glycocine obtained by this method was about 28 per cent. of theory.

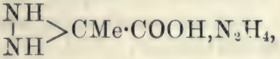
Calcium Orthotolylglycocine, $(C_9H_{10}NO_2)_2Ca + 3H_2O$.—This salt is prepared by a method similar to that used in the preparation of calcium orthophenylglycocine (compare Abstr., 1889, 1068). When crystallised from water, it forms flat, glistening needles which are insoluble in absolute alcohol. On dry distillation with calcium formate, a product was obtained which appears to be orthotolindole (compare Raschen, Abstr., 1887, 956).

Calcium α-naphthylglycocine, $(C_{12}H_{10}NO_2)_2Ca + 3H_2O$, is obtained by dissolving α-naphthylglycocine in dilute ammonia, and precipitating the warm solution with calcium chloride. When crystallised from dilute alcohol, the salt forms clusters of flat needles. On heating with calcium formate, a substance was obtained which resembles Schlieper's α-naphthindole (*ibid.*, 963) in crystallising in needles, but has a lower melting point, 163°.

Phenylglycocineparacarboxylic acid, $C_9H_9NO_4$, is obtained by boiling for several hours a mixture of paramidobenzoic acid (25 grams), chloracetic acid (20·6 grams), and sodium carbonate (32·8 grams), dissolved in water (1 litre). On acidifying the cooled solution, a yellow powder (yield 30·2 grams) is precipitated, and this, on recrystallisation from water, forms a crystalline mass which melts with decomposition at 219—221°. The barium salt, $C_6H_7NO_4Ba + 4H_2O$, and the calcium salt, $C_9H_7NO_4Ca + 3H_2O$, are white, crystalline powders; the copper salt, $C_9H_7NO_4Cu + 3H_2O$, is a dark-green amorphous powder.

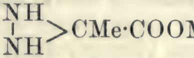
G. T. M.

Constitution of Diazo-fatty Acids. By T. Curtius (*Ber.*, **23**, 3036—3037).—*Hydrazine α-hydrazopropionate*,



$$\begin{matrix}NH\\|\\NH\end{matrix}>CMe\cdot COOH,N_2H_4,$$

is obtained from hydrazine hydrate and pyruvic acid as a colourless, crystalline powder melting at 116°.

Methyl α-hydrazopropionate,  $\begin{matrix}NH\\|\\NH\end{matrix}>CMe\cdot COOMe$, is prepared in a similar manner from methyl pyruvate and hydrazine hydrate; it melts at 82°, and on treatment with mercuric oxide yields a methyl α-diazopropionate, $N_2CMe\cdot COOMe$, which boils at 53—55° under a pressure of 32 mm. The same compound has previously been prepared in small quantities from methyl α-amidopropionate and sodium nitrite. This result proves conclusively that in the diazo-fatty acids the two nitrogen atoms are linked to the same carbon atom.

J. B. T.

Action of Bromine on Angelic Acid and Maleïc Acid. By R. Fittig (*Annalen*, **259**, 1—40).—When Wislicenus was engaged in developing his theory of the rotation of atomic configurations, there were on record various observations made by the author and his pupils which were not in accordance with the new theory; many of the author's experiments were, therefore, repeated by Wislicenus with results which agreed better with his theoretical views, but which were totally at variance with those previously obtained by the author.

The author has repeated some of the experiments in question with the utmost care, and has shown that his previous statements are absolutely correct in every detail.

One of the most important points of difference which received attention was the investigation of the action of bromine on angelic acid. It had been stated by Fittig and Pagenstecher (Abstr., 1878, 455) that angelic acid combines with bromine, yielding tiglic acid dibromide as principal product; a small quantity of another substance, which could not be obtained in a pure condition, being produced at the same time.

Wislicenus and Pückert (Abstr., 1889, 587) found, on the other hand, that tiglic acid dibromide is not produced by the action of bromine on angelic acid; they obtained a substance with totally different properties, the investigation of which proved to their minds its complete dissimilarity from tiglic acid dibromide.

Now, as the author had obtained 27 grams of pure tiglic acid dibromide from 15 grams of angelic acid, and had proved the identity of the product with the substance obtained directly from tiglic acid, not only by a general, but also by a crystallographic, examination, and as, furthermore, his observations had been confirmed by Schmidt (*Annalen*, **208**, 252), Wislicenus' results were received with great astonishment, and the reinvestigation of the subject was commenced.

In the first place, a sample of the so-called angelic acid dibromide, prepared by Wislicenus and Pückert, was examined by the author, and found to be wanting in all the properties of a pure chemical compound; it seemed to consist principally of tiglic acid dibromide, mixed, however, with various substances, amongst others calcium compounds and resinous matters.

The author then began various experiments on the action of bromine on angelic acid. The acid employed melted at 44°, and as it had been kept for 12 years, it would seem that angelic acid does not become converted into tiglic acid on keeping, as is supposed by Schmidt. The acid was very carefully dried, and then distilled; it boiled at 185°, and underwent no change into tiglic acid, either when boiled or when distilled with steam. Wislicenus and Pückert's statement that pure angelic acid is converted into tiglic acid on boiling with water cannot therefore be confirmed. The pure angelic acid was treated with bromine in carbon bisulphide solution at 0° in diffused daylight, moisture being carefully excluded; several experiments were made under various conditions, in some cases the solution of the acid being added to the bromine solution, in others the process being reversed.

In all the experiments, which are described in great detail, a large quantity of tiglic acid dibromide was obtained, and the identity of the product with the dibromide prepared directly from tiglic acid was proved, by direct comparison as well as by a crystallographic examination.

These results show that the statements published by the author more than 12 years ago are absolutely correct in every detail; it may, therefore, be considered as proved, that when angelic acid is treated with bromine in carbon bisulphide solution at 0° in diffused daylight, it is almost completely converted into tiglic acid dibromide in the course of a few hours.

A number of careful experiments were also made in order to investigate the behaviour of angelic acid with bromine in absence of sunlight; it was found that, whatever the conditions, the principal product is always tiglic acid dibromide, but that another substance, which is not produced from tiglic acid under the same conditions, is also formed in small quantities. Although, then, the formation of tiglic acid dibromide takes place quickly in presence of diffused sunlight at 0°, and the yield is almost quantitative, in the dark the reaction takes place only very slowly, even at the ordinary temperature, and a larger quantity of a more readily soluble compound is produced. The presence of this readily soluble compound has great influence on the behaviour of the tiglic acid dibromide; it makes it much more readily soluble in all ordinary solvents, retards its crystallisation, and causes it to deliquesce with water. The nature of this bye-product could not be determined, but it is probably an isomeride of tiglic acid dibromide; the substance prepared by Wislicenus and Pückert evidently contains both these compounds.

After referring to several minor errors in the statements and results published by Wislicenus, the author criticises Wislicenus' experiments on the action of bromine on maleïc acid, and points out that the conclusions drawn therefrom by Wislicenus are directly opposed to the present theories.

In conclusion, the author protests against the way in which Wislicenus is accustomed to trust to his memory alone in referring to the literature of chemistry; in many cases, the author and others are made to state and affirm in their papers, the references to which are all given, just what Wislicenus himself believes at the time, whereas the actual statements are sometimes the exact contrary and sometimes do not appear at all in the articles referred to, but exist solely in Wislicenus' imagination. F. S. K.

Syntheses of Nitriles and of β-Ketonic Ethers. By L. BOUVEAULT (*Compt. rend.*, **111**, 531—533).—It has previously been shown (Abstr., 1889, 841) that the products of the action of sodium on propionitrile in presence of ether contain the compound

$$NH\colon CEt\cdot CMeNa\cdot CN,$$

and it follows that the mixed compound obtained by the action of sodium on the two nitriles $R\cdot CH_2\cdot CN$ and $R'\cdot CN$ (*J. prakt. Chem.* [2], **39**, 188, 230, 245) will have the constitution $NH\colon CR'\cdot CRNa\cdot CN$. If this derivative is treated with an alkyl iodide, as in the case of propionitrile, it will form the compound $R'\cdot C(NH)\cdot CR''R\cdot CN$, which will be converted by hydrochloric acid into a β-ketonic nitrile $R'\cdot CO\cdot CR''R\cdot CN$. These nitriles can readily be converted into alkyl salts by dissolving them in the corresponding alcohol and saturating the solution with dry hydrogen chloride.

Methylic methylpropionylacetate, $COEt\cdot CHMe\cdot COOMe$, boils at 185°, and is identical with Israel's methyl propionylpropionate (*Annalen*, **231**, 197); *methyl dimethylpropionylacetate*, $COEt{\cdot}CMe_2{\cdot}COOMe$, is a colourless liquid which has a camphoraceous odour and boils at 188—188·5° (corr.) under a pressure of 760 mm.

These changes are quite general, and all the β-ketonic alkyl salts can be obtained from their nitriles.

Methyl methylpropionylacetate shows powers of condensation similar to those of ethyl acetoacetate; it combines with aniline to form amethylethyloxyquinoline melting at 295°, and insoluble in ether; water, methyl alcohol, and carbanilide are formed at the same time.

The β-ketonic nitriles, when heated in sealed tubes with hydrochloric acid, yield ketones, a reaction discovered by E. v. Meyer. The nitrile $COR{\cdot}CR'R''{\cdot}CN$ will yield the ketone $COR{\cdot}CHR'R''$, and in this way all the ketones can be obtained in which the two atoms of carbon united to the carbonyl are not both tertiary.

C. H. B.

Syntheses with Ethyl Sodiocarbamate. By F. KRAFT (*Ber.*, **23**, 2785—2787).—When ethyl carbamate is treated with finely-divided sodium in ethereal solution, it is converted into a white, amorphous sodium compound, $NHNa{\cdot}COOEt$, which is very hygroscopic, has an alkaline reaction, and is reconverted by dilute acids into ethyl carbamate. The displacement of sodium by methyl does not take place very readily, it being necessary to heat the mixture of ethyl sodiocarbamate and methyl iodide diluted with ether, at 110°, in a sealed tube. The product, after separating the sodium iodide and evaporating the ether, is fractionated, and yields regenerated ethyl carbamate and ethyl methylcarbamate, $NHMe{\cdot}COOEt$, boiling at 170°.

Ethyl chlorocarbonate acts on the sodium compound suspended in ether at the ordinary temperature. After the reaction is over, sufficient water is added to dissolve the sodium chloride formed, the solution is extracted with ether, and the extract, after evaporation of the ether, is fractionated. At 110°, a solid substance commences to separate, but at 210—215° an oil passes over, leaving a solid residue which consists of cyanuric acid. On refractionating the oil, more cyanuric acid is obtained, but the greater portion passes over at 215°, and solidifies after a time to a crystalline mass closely resembling ethyl carbamate, and having the same melting point of 50°, but it boils 35° higher, and does not volatilise on remaining in the exsiccator. Its analysis agrees with the formula $C_6H_{11}NO_4$, and it is therefore, as expected, *ethyl imidodicarboxylate*, $NH(COOEt)_2$.

H. G. C.

Methyl Cyanosuccinate and Cyanotricarballylate. By L. BARTHE (*Compt. rend.*, **111**, 343—345).—Methyl sodiocyanacetate is prepared by the action of sodium methoxide on methyl cyanacetate in presence of excess of methyl alcohol, the product being heated in a water-bath for several hours with methyl monochloracetate. The liquid is then mixed with water, and the reddish oil which separates is dissolved in ether, dried, and distilled.

The fraction which boils at 196—204° under a pressure of 45 mm. is *methyl cyanosuccinate*, $COOMe{\cdot}CH_2{\cdot}CH(CN){\cdot}COOMe$, an oily, colourless liquid, insoluble in water, but soluble in methyl and ethyl alcohols and in alkalis. The fraction boiling at 215° under the same pressure solidifies after some hours, and is purified by recrystallisation from methyl alcohol. It is *methyl cyanotricarballylate*, $CN\cdot C(CH_2\cdot COOMe)_2\cdot COOMe$, and forms white, prismatic crystals which melt at 46·5—47·5°, and are soluble in ethyl and methyl alcohols and in ether, but insoluble in water and alkalis. It is formed in the same manner as ethyl cyanotricarballylate (Abstr., 1888, p. 937), and can, in fact, be obtained by the direct action of methyl monochloracetate on methyl sodiocyanosuccinate. C. H. B.

Ethyl Allylcyanosuccinate. By L. Barthe (*Compt. rend.*, **111**, 342—343).—20 grams of ethyl cyanosuccinate is mixed with a solution of 2·3 grams of sodium in 60 grams of alcohol, 16 grams of allyl iodide is added, and the liquid is heated in a water-bath for about 30 hours in an apparatus with a reflux condenser. The product, after separation of the alcohol by distillation, is extracted successively with water and ether. The latter dissolves the ethyl allylcyanosuccinate, which is obtained as a colourless, oily liquid boiling at 207—210° (corr.) under a pressure of 35 mm. C. H. B.

The so-called "Sulphite Liquor" and the Rotation of Glyconic, Galactonic, and Rhamnonic Acids. By F. Weld, J. B. Lindsay, W. Schnelle, and B. Tollens (*Ber.*, **23**, 2990—2992).—The so-called "sulphite-liquor" obtained in the cellulose works is a very slightly milky liquid, which, besides calcium sulphate and potassium sulphide, contains much organic matter. On distilling the liquid with sulphuric or hydrochloric acid it yields furfuraldehyde and furfuramide, showing the presence of pentoses (xylose). The quantity of the latter is small. If the liquid obtained after hydrolysis with sulphuric acid be separated from gummy matters by precipitation with alcohol, it yields, on treatment with phenylhydrazine, considerable quantities of mannosephenylhydrazone. By the action of nitric acid, the evaporated liquor yields mucic acid, showing the presence of galactan or galactose, and the presence of vanillin has also been shown by the phloroglucinol reaction.

The specific rotatory power of certain acids of the sugar group, and of their calcium salts, has also been examined, with the following results (see also Fischer, Abstr., 1890, 1398):—Gluconic acid.—With calcium gluconate, $[\alpha]_D = +7°$. If this salt is dissolved in water and an equivalent quantity of hydrochloric acid, it shows, after 10 minutes, a specific rotatory power of $+2—3°$, calculated as free gluconic acid, $C_6H_{12}O_7$; after 5 days, the rotation remains constant, $[\alpha]_D = +9·8—10·4°$. If the mixture of calcium gluconate and hydrochloric acid is heated at first for half an hour at 100°, $[\alpha]_D = +19°$, and this rotation is reduced to one half in two to three weeks. Galactonic acid.—Calcium galactonate, and an equivalent of hydrochloric acid, gave, at first, $[\alpha]_D = -10·56°$, and after 2—3 weeks, $[\alpha]_D = -46·82°$. After heating for half an hour on the water-bath, $[\alpha]_D = -57·84°$, which, after remaining for 14 days, sank to $-53·36°$. Crystallised galactonic lactone gave, at first, $[\alpha]_D = -58·29$, which scarcely altered on being kept for a time. Rhamnonic acid.—With great difficulty, strontium rhamnonate, $(C_6H_{11}O_6)_2Sr + 7$ or $7\frac{1}{2}H_2O$, and an ammonium salt were obtained in a crystalline condition. The former, when dissolved in hydrochloric acid, gave, at first, $[\alpha]_D = -7\cdot67°$, and after 5—6 days, the constant number, $[\alpha]_D = -29\cdot21°$, and after heating, $-34\cdot30°$, which sank in 5—6 days to $-30\cdot12°$. Rhamnonic lactone gave, immediately after solution, the result $[\alpha]_D = -34\cdot26$, calculated like the foregoing, for rhamnonic acid, $C_6H_{12}O_6$. In three days the rotation had scarcely altered. H. G. C.

Constitution of Benzene and Naphthalene. By A. Claus (*J. pr. Chem* [2], **42**, 458—469).—A reply to the criticisms which Bamberger has recently passed on Claus' formulæ (compare this vol., p. 1299). A. G. B.

Substitution in Aromatic Hydrocarbons. By O. Srpek (*Monatsh.*, **11**, 429—432).—With the object of obtaining parabromobenzyl chloride, bromine (126 grams) was slowly added, in the dark, to a mixture of benzyl choride (100 grams) and iodine (5 grams). The solid product, after many recrystallisations from alcohol, melted at 59°, and consisted of a mixture of parabromobenzyl bromide, which melts at 61°, with a small quantity of a compound containing chlorine in both the nucleus and the side chain. A similar result was obtained when chlorine acted on parabromotoluene in direct sunlight. The crystalline product obtained melted at 52°, and consisted chiefly of parabromobenzyl bromide. The formation of this compound is easily accounted for if one supposes that chlorobenzyl chloride is simultaneously formed; examination of oily bye-products points to such being the case. G. T. M.

Derivatives of Orthodibromobenzene. By F. Schiff (*Monatsh.*, **11**, 329—349).—A more satisfactory method of obtaining orthodibromobenzene than those described by Riese (this Journal, 1873, 63), and Körner (*ibid.*, 1876, i, 214), is as follows:—Bromobenzene is added gradually to 6—7 times its weight of well-cooled nitric acid of sp. gr. 1·53, and the resulting nitro-compounds crystallised from alcohol, when the chief product, paranitrobromobenzene, melting at 126—127°, first separates (yield 80 per cent. of theory). On heating this compound with the corresponding quantity of bromine and ferric chloride for 50 hours at 85—90° (compare Scheufelen, Abstr., 1886, 340), para-orthonitrodibromobenzene, melting at 58—59° (yield 90 per cent. of theory), is obtained, and this, on elimination of the nitro-group, is converted into orthodibromobenzene, which, when pure, boils at 224°, solidifies at −5°, and melts at −1° (compare Meyer and Wurster, this Journal, 1874, 757, 758). Pure metadibromobenzene, after being frozen in a mixture of solid carbonic anhydride and ether, melts at 1—2°.

When dibromonitrobenzene is treated with ten times its weight of concentrated nitric acid, of sp. gr. 1·53, and the mixture is warmed in a water-bath for 12 hours, two dibromodinitrobenzenes (α- and β-)

are formed, and may be readily separated by fractional crystallisation from acetic acid.

α-Dibromodinitrobenzene is less soluble in acetic acid and in alcohol than the β-compound. It crystallises from alcohol in needles melting at 114—115°. On reduction with tin and hydrochloric acid, it is converted into dibromodiamidobenzene, which crystallises from dilute alcohol in needles melting, with decomposition, at 137°. On treatment with alcoholic ammonia at 110—120°, it gives a dibromonitroaniline, crystallising from alcohol in orange-yellow needles melting at 204—205°, and this, by elimination of the amidogen group, is converted into the original nitrodibromobenzene, and seems to be identical with the dibromonitraniline melting at 202°, obtained from dibromaniline, $[Br_2 : NH_2 = 1 : 2 : 4]$, by acetylation, nitration, and subsequent elimination of the acetyl group; α-dibromodinitrobenzene has, consequently, the constitution $[Br_2 : (NO_2)_2 = 1 : 2 : 4 : 5]$.

β-Dibromodinitrobenzene is very soluble in alcohol and in acetic acid, and crystallises from the former in needles, and from the latter and from carbon bisulphide in small, rhombic plates $[a : b : c = 1 : 0{\cdot}8541 : 0{\cdot}5700]$. On treatment with alcoholic ammonia, it gives a dinitrobromaniline, which crystallises from alcohol in yellow needles melting at 153°; this is identical with the compound obtained by Leymann (Abstr., 1882, 1057) by the bromination of metadinitraniline [1 : 3 : 4]. The compound has, consequently, the constitution $[Br_2 : (NO_2)_2 = 1 : 2 : 3 : 5]$.

On diazotising the dibromaniline above-mentioned, dibromophenol, $[Br_2 : OH = 1 : 2 : 4]$, which may be readily sublimed, and crystallises from water in needles melting at 79—80°, is obtained.

G. T. M.

Change of Propyl into Isopropyl in the Cumine Series. By O. Widman (*Ber.*, **23**, 3080—3088).—*Para-ethylpropylbenzene*, $C_6H_4EtPr^{\alpha}$, prepared by heating a mixture of parabromopropylbenzene and ethyl bromide with sodium, boils at 202—205° (corr.), and has a specific gravity of 0·867 at 19°. It yields terephthalic acid as sole produce of oxidation with alkaline permanganate solution, whilst with dilute nitric acid, propylbenzoic acid, together with a little ethylbenzoic acid, is formed.

By the action of sulphuric acid on ethylpropylbenzene, a mixture of two sulphonic acids is obtained; these are converted into sulphonamides, and separated by repeated crystallisation from alcohol.

Para-ethylpropylbenzene-α-sulphonamide,

$$C_6H_3EtPr^{\alpha}{\cdot}SO_2NH_2\ [Et : Pr : S = 1 : 4 : 6],$$

crystallises from dilute alcohol, or from a mixture of benzene and light petroleum, in long, flat needles melting at 112—113°; on oxidation with chromic acid solution, it yields sulphonamidethylbenzoic acid, $[Et : COOH : S = 1 : 4 : 6]$.

Para-ethylpropylbenzene-β-sulphonamide, $[Et : Pr : S = 1 : 4 : 5]$, is deposited in cubical crystals which melt at 108°, and on oxidation give sulphonamidepropylbenzoic acid. The oxidation of an ethyl group in the para-position does not, therefore, bring about the change of propyl into isopropyl; in this respect the ethyl group resembles the propyl, isopropyl, and acetyl groups; consequently, the rearrangement to isopropyl appears to take place exclusively in the paramethyl derivatives. J. B. T.

Behaviour of Phenols and Hydroxy-acids towards the Alkali Hydrosulphides. By F. Fuchs (*Monatsh.*, **11**, 363—372).—The author has previously shown (Abstr., 1889, 496) that the hydroxylic hydrogen of hydroxy-acids and phenols, derived from aromatic hydrocarbons, is not displaced by metal, on treatment with an alkali hydrosulphide. The hydroxy-acids of the fatty series, such as malic, citric, and tartaric acids, behave in a precisely similar way; tetra- and penta-methylphloroglucinols decompose hydrosulphides as if they were monobasic acids, an action which the presence of carbonyl groups may possibly determine; on the other hand, tetra- and penta-ethylphloroglucinols have no such action, although the substitution of bromine in the β-position brings about decomposition of the hydrosulphide. This difference in the behaviour of methyl and ethyl derivatives appears to depend on the relative weights of the molecules.

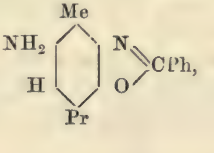
Ortho- and meta-nitrophenols have no action on sodium hydrosulphide, whilst paranitrophenol decomposes it. The substitution of a nitro-group in the ortho- or meta-position in a phenol seems, therefore, not to affect the replaceability of the hydroxylic hydrogen, whilst its substitution in the para-position does. This view is confirmed by the behaviour of nitroeugenol, in which the nitro-group is ortho- to the hydroxyl.

Tribromoresorcinol behaves as a monobasic acid, only one of the hydroxylic hydrogen atoms being displaced by sodium from the hydrosulphide. When one hydroxyl group is displaced by ethoxyl, no such substitution occurs. The action of some other nitro- and halogen-substituted phenols on sodium hydrosulphide has been determined, and the results depend both on the number and the position of the substituted groups, although no general conclusions can yet be drawn. G. T. M.

Constitution of Thymol and Cymene Derivatives. By G. Mazzara (*Gazzetta*, **20**, 140—149).—*Dinitrothymyl benzoate*,

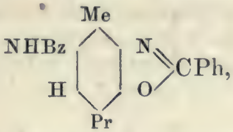
$$C_6HMePr(NO_2)_2\cdot OBz \; [1:4:2:6:3],$$

prepared by heating the corresponding dinitrothymol with benzoic chloride for about two hours at 160° to 180°, crystallises from alcohol in yellow, rhombohedral plates, melts at 127—128°, and dissolves readily in light petroleum and benzene.

Amidobenzamidothymol, 

prepared by reducing

the preceding compound with tin and hydrochloric acid, crystallises from alcohol in yellow plates and from light petroleum in prisms, melts at 106—108°, and is tinged faintly violet by light. It is not altered by boiling with hydrochloric acid or with dilute (20 per cent.) sulphuric acid. The *platinochloride* crystallises from alcohol in yellow needles which decompose at 215°.

Benzoylamidobenzamidothymol,  prepared by heating a solution of the preceding compound in benzene with benzoic chloride, crystallises from alcohol in bulky, white needles and melts at 174—175°. It may be boiled with hydrochloric or dilute sulphuric acid without change.

The formation of the above benzenylamido-derivatives is in accordance with the hypothesis that in dinitrothymol one of the nitro-groups is in the ortho position with respect to the hydroxyl. The author is also investigating the action of acetic anhydride on the corresponding amido-derivative with the view of obtaining a further confirmation of this constitution by the formation of an ethenyl derivative.

Dinitrothymyl acetate. $C_6HMePr(NO_2)_2{\cdot}OAc$ [1 : 4 : 2 : 6 : 3], prepared by heating dinitrothymol with acetic chloride, crystallises from alcohol in prismatic tufts, melts at 85°, and dissolves in light petroleum, ether, and chloroform. The author considers that the dinitrocymene melting at 54°, previously described (Abstr., 1890, 753), has the constitution $[Me : NO_2 : Pr : NO_2 = 1 : 2 : 4 : 6]$ and that the liquid and solid dinitrobromocymenes prepared by Fileti and Crosa (Abstr., 1889, 493) have respectively the constitutions

$$[Me : Br : Pr : NO_2 : NO_2 = 1 : 2 : 4 : 5 : 6 \text{ and } = 1 : 2 : 4 : 5 : 3].$$

S. B. A. A.

Constitution of Thymoquinone and Carvacrol Derivatives. By G. MAZZARA (*Gazzetta*, **20**, 183—190).—*Dinitrocarvacrol*,

$$C_6HMePr(NO_2)_2{\cdot}OH\ [1 : 4 : 3 : 5 : 2],$$

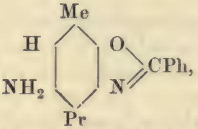
prepared by Carstanjen (Abstr., 1877, 614), crystallises from light petroleum in tufts of yellowish needles which turn red even in diffused light and melt at 117°. It dissolves in dilute alcohol. The *benzoyl* derivative, $C_6HMePr(NO_2)_2{\cdot}OBz$ [1 : 4 : 3 : 5 : 2], prepared like the corresponding thymol derivative, crystallises from alcohol in large, yellow, prismatic plates which melt at 98—100°, and turn brown when exposed to the light.

Diamidocarvacrol, $C_6HMePr(NH_2)_2{\cdot}OH$, is prepared by heating dinitrocarvacrol (15 grams) for about an hour, with tin (47 grams) and fuming hydrochloric acid (145 grams). The *hydrochloride* forms white plates which are coloured violet by exposure to light; the base is a red powder which softens at about 190°.

Nitroamidocarvacrol benzoate,

$$C_6HMePr(NO_2)(NH_2){\cdot}OBz\ [1 : 4 : 3 : 5 : 2],$$

is prepared by heating dinitrocarvacrol benzoate (10 grams) for about an hour with tin (22 grams) and fuming hydrochloric acid (70 grams). It crystallises in rose-coloured scales which have a metallic lustre. It forms a white sublimate at 200°, softens at 230°, and melts at 280—283°. The *platinochloride*, $(C_{17}H_{18}N_2O_4)_2,H_2PtCl_6$, crystallises in yellow needles which lose part of their acid at 30—40°. The physical properties of this compound and the absence of any nitrobenzenyl derivative, together with the formation of a benzoyl-derivative (not yet described) with benzoic chloride, indicate that the nitro-group in this compound is in the ortho-position with regard to the hydroxyl.

Amidobenzamidocarvacrol, 

, is obtained by boiling dinitrocarvacrol benzoate with tin and hydrochloric acid for 5 hours. It crystallises from alcohol in violet prisms which soften at 125° and melt at 130—132°. The formation of a benzenyl derivative from dinitrocarvacrol benzoate and of a hydroxythymoquinone by the oxidation of the amido-derivative shows that in dinitrocarvocrol one of the nitro-groups is in the ortho-position and the other in the para-position with respect to the hydroxyl.

Phenylazo- and phenyldisazo-carvacrol (Abstr., 1885, 1132), which respectively yield thymoquinone and hydroxythymoquinone on oxidation, will accordingly have the constitutions [Me : OH : Pr : N_2Ph = 1 : 2 : 4 : 5] and [Me : OH : N_2Ph : Pr : N_2Ph = 1 : 2 : 3 : 4 : 5].

S. B. A. A.

Action of Chloral on Resorcinol and of Aldehyde on Pyrogallol. By H. CAUSSE (*Bull. Soc. Chim.*, [3], **3**, 861—867).—Resorcinol (100 grams) and sodium hydrogen sulphate (20 grams) are dissolved in water (1 litre) and chloral hydrate (50 grams) is added to the mixture, which after some time deposits colourless, oily crystals; if warmed at 100°, yellow crystals are deposited resulting from the dehydration of the former. The colourless crystals are insoluble in water and in benzene, but dissolve in alcohol or ether, whilst their solutions in alkaline hydroxides exhibit a remarkable fluorescence. At 250°, they become yellow, and decompose without fusion. With acetic anhydride, this substance yields a crystalline diacetyl derivative, which melts at 252° with decomposition. Analysis gives the formula $C_{14}H_{12}O_6$, and the same compound resulting from the heating at 100° of equal parts of resorcinol and of glyoxylic acid points to its having the constitution $COOH·CH(O·C_6H_4·OH)_2$.

Pyrogallol (50 grams), sulphuric acid (5 grams), aldehyde (25 c.c. of a 10 per cent. solution) and water, (500 grams) are heated at 100° for several hours and successive quantities of 10 per cent. sulphuric acid are added, when crystals separate out, and by the addition of more aldehyde and acid further crops are obtainable. From the mass of crystals, the colourless are alone separated and recrystallised from alcohol, separating as small, colourless needles having the composition $C_8H_8O_3$, containing 2 mols. H_2O, which are successively lost at 30° and 80°. The substance is insoluble in water, benzene, and chloroform, slightly soluble in alcohol and ether, but is dissolved easily by alkaline hydroxides. At 260°, it decomposes, and yields pyrogallol at a slightly elevated temperature. It has the constitution $CHMe{:}O_2{:}C_6H_3{\cdot}OH$; with acetic anhydride, it forms a monacetyl derivative which crystallises in white prisms which melt at 280°.

T. G. N.

Formation of Ethereal Salts and Amides in presence of Water and Alkali. By O. HINSBERG (*Ber.*, **23**, 2962—2965).—It has been shown by Baumann and his pupils (Abstr., 1887, 228; 1888, 1296; 1889, 370) that benzoic chloride may be used for detecting the hydroxyl-, amido-, and imido-groups in certain compounds by acting on them with that reagent in aqueous solution in presence of alkali. This reaction was, however, first employed for the preparation of benzoyl compounds by Schotten (Abstr., 1885, 176).

The author has further examined the action of other acid chlorides and of acetic anhydride under similar conditions, and finds that complete acetylation of the primary and secondary amido-bases and the aromatic diamido-bases readily takes place on shaking them with acetic anhydride and iced water. Phenylacetic chloride acts on monhydric alcohols and phenols, and primary and secondary amido-bases belonging to both the fatty and aromatic groups in the same manner as benzoic chloride. Diamines and polyvalent alcohols, such as glucose, can also be readily converted into phenylacetic derivatives.

Phenylsulphonic chloride is without action on tertiary amines, but acts on both secondary and primary amines very readily. The former yield solid or viscous products, insoluble in acids and alkalis, whilst the latter form sulphonamides which are readily soluble in alkalis. This reaction may therefore be employed to ascertain whether an amido-compound belongs to the primary, secondary, or tertiary series, and also forms a ready method for the separation of a mixture of members of the three classes.

If the tertiary base is volatile with steam, the mixture of bases after treatment with phenylsulphonic chloride and alkali and approximate neutralisation, may be distilled in a current of steam. The sulphonamide of the secondary compound then remains as an insoluble precipitate in the residue, and may be filtered off, and the primary compound obtained from the filtrate by precipitation with hydrochloric acid. If the tertiary base is not volatile with steam, the mixture is extracted with ether and the tertiary base separated from the sulphonamide of the secondary base by shaking the ethereal solution with dilute hydrochloric acid. The sulphonamide of the primary base is obtained by precipitating with hydrochloric acid the aqueous solution remaining after the extraction with ether. To reconvert the sulphonamides into the bases, they are heated with hydrochloric acid in a sealed tube at 160°.

The reaction with phenylsulphonic chloride is not given by amido-compounds which already contain an acid or other strongly negative radicle, such as the acid amides and halogen and nitro-derivatives of the amido-bases. On the other hand, complicated substances such as fibrin and peptone yield white products, soluble in alkalis, which have, however, not at present been obtained in the crystalline form.

H. G. C.

Polemical. By O. REBUFFAT (*Gazzetta*, **20**, 122—123).—A controversial note in reference to the papers published by A. Bischoff (*Ber.*, **22**, 1774) and A. Bischoff and A. Hausdorfer (*ibid.*, 1795) on the action of aniline on chloracetic acid.

S. B. A. A.

The Condensation Products of Aromatic Aldehydes with Aromatic Amines. By A. HANTZSCH (*Ber.*, **23**, 2773—2776).—These condensation products, of which the best known is benzylidine-aniline, CHPh⁚NPh, resemble the oximes, inasmuch as they contain a carbon and a nitrogen atom united together by double linkage, and it seemed, therefore, important to determine, if possible, whether these also exist in isomeric forms. An attempt was first made to convert benzylidine-aniline into an isomeric compound by treating it with bromine, under which conditions the plane symmetrical tolane dibromide is converted into the axial symmetrical isomeride. The reaction was carried out in carbon bisulphide solution, and a yellow, amorphous compound obtained, which was shown by analysis to be *benzylidine-aniline dibromide*, $C_{13}H_{11}NBr_2$. It melts with decomposition at about 142°, is insoluble in water and ether, but dissolves in cold alcohol. It is very readily decomposed, but, instead of re-forming benzylidine-aniline, it splits up into benzaldehyde and parabromaniline. This takes place most readily on heating with pyridine. With reducing agents, it loses hydrogen bromide and not bromine, and is converted by sodium hydrogen sulphite into the additive product $2C_6H_5{\cdot}CHO + 2C_6H_4Br{\cdot}NH_2 + SO_2$, corresponding with the aniline compound described by Schiff (Abstr., 1882, 304).

Benzylidine-aniline also yields a *di-iodide*, $C_{13}H_{11}NI_2$, obtained by mixing the former with iodine in benzene solution. It forms well-developed, dark brown needles, which melt at 110° with decomposition, do not yield iodaniline on heating with pyridine, and on reduction re-form benzylidine-aniline. No isomeride of the latter can, therefore, be obtained in this manner.

Attempts were also made to obtain isomeric condensation products from substituted benzaldehydes and substituted anilines, but without success.

H. G. C.

Orthohydroxybenzylamine. By F. TIEMANN (*Ber.*, **23**, 3016—3018; compare Goldschmidt and Ernst, Abstr., 1890, 1411).—*Salicylmetahydrazobenzoic acid*, $OH{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$ [OH : CH = 1 : 2; NH : COOH = 1 : 3], is prepared from salicylaldehyde and metahydrazinebenzoic acid; it crystallises from dilute alcohol in needles, melts at 195°, and is insoluble in water. On treatment with zinc-dust and dilute sulphuric acid, *orthohydroxybenzylamine*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$, and metamidobenzoic acid are formed; they may be separated by adding a slight excess of sodium carbonate to the acid solution, and extracting with ether; after evaporation, the residual amine is purified by dissolving it in benzene, and precipitating with light petroleum; light yellow crystals separate, which melt at

125°, and sublime at a much lower temperature. It is soluble in water, alcohol, ether, benzene, and alkalis, and gives a deep violet-blue colour with ferric chloride. Characteristic salts are obtained by treatment with acids. The *oxalate* crystallises in lustrous, white plates. The amine may also be prepared by the reduction of salicylic oxime with sodium amalgam in dilute sulphuric acid solution.

J. B. T.

Possibility of Existence of an "Asymmetrical Nitrogen Atom." By F. KRAFT (*Ber.*, **23**, 2780—2784).—According to the hypothesis of Hantzsch and Werner, it is possible that nitrogen compounds of the general formula NXYZ may exist in two optically isomeric forms, and the author has, therefore, investigated derivatives of ammonia, hydrazine, and hydroxylamine, with a view to obtaining such isomerides.

For the ammonia derivative, ethylbenzylamine, $NHEt\cdot CH_2Ph$, was chosen, as it yields a crystalline tartrate. It was prepared by heating ethylamine with benzyl chloride and a little alcohol in a sealed tube at 110°, and forms a colourless oil which has an ammoniacal odour, and boils at 194° (corr.). Its *platinochloride*, $(C_9H_{13}N)_2,H_2PtCl_6$, crystallises in prisms. In addition to the secondary base, a quantity of *ethyldibenzylamine*, $NEt(CH_2Ph)_2$, is also obtained; it is an oily liquid boiling at 306°, whose *platinochloride*, $(C_{16}H_{19}N)_2,H_2PtCl_6$, is a pale yellow, amorphous precipitate. The attempt to separate ethylbenzylamine tartrate into two isomerides both by addition of conine tartrate and by fractional crystallisation, was without success. Negative results were also obtained in the case of paratolylhydrazine tartrate. The conclusion cannot, however, be drawn from these facts that optical isomerides of these compounds do not exist, for the tartrate method is not always successful even with compounds containing an asymmetrical carbon atom. Thus, the author finds that α-phenylethylamine, $CHMe\cdot Ph\cdot NH_2$, obtained by the reduction of acetophenonoxime, cannot be split up into its optical isomerides by this method.

Finally, it is shown that both benzileoximes, on reduction, yield one and the same diphenylhydroxyethylamine, $NH_2\cdot CHPh\cdot CHPh\cdot OH$, previously obtained from the α-monoxime by Polonowska (Abstr., 1887, 492).

H. G. C.

Action of Amines of the Benzene Series and of Phenylhydrazine on β-Ketonic Nitriles. By L. BOUVEAULT (*Compt. rend.*, **111**, 572—574).—Methylpropionylacetonitrile combines with orthotoluidine to form a well crystallised compound, which melts at 125°, and dissolves in alcohol, but is insoluble in ether or water. With β-naphthylamine, the nitrile yields a compound which crystallises in needles melting at 121°, and dissolves in benzene, but is almost insoluble in ether. Mesidine yields a similar product melting at 114—115°. Methylaniline does not combine with methylpropionylacetonitrile, but, on the other hand, the higher homologue of the latter combines readily with orthotoluidine, forming a liquid boiling at 266°, but analogous to the products already described. From these results, the author concludes that the aniline derivative has the constitution $PhN{:}CEt{\cdot}CHMe{\cdot}CN$, and he calls it *phenylimidomethylpropionylacetonitrile.* The reaction is general, and the nitriles $R{\cdot}CO{\cdot}CR'R''{\cdot}CN$ yield derivatives of the formula $R'''N{:}CR{\cdot}CR'R''{\cdot}CN$.

The action of phenylhydrazine depends on the constitution of the nitrile; if the latter belongs to the type $R{\cdot}CO{\cdot}CR'R''{\cdot}CN$, a hydrazone is formed, $NHPh{\cdot}N{:}CR{\cdot}CR'R''{\cdot}CN$, but if it belongs to the type $R{\cdot}CO{\cdot}CHR'{\cdot}CN$, a derivative of pyrazole is obtained. Possibly in the second case there is intermediate formation of a hydrazone. Methyl propionylacetonitrile yields *phenylethylmethylamidopyrazole* [1 : 3 : 4 : 5], which crystallises in large, colourless, hexagonal prisms melting at 81°, and boiling at 330° without decomposition. It is very soluble in most of the neutral solvents, but not readily in benzene or petroleum. It is a stronger base than the preceding compounds, and its acetate is only partially decomposed by water. When heated with hydrochloric acid in sealed tubes at 120°, the base undergoes no change. With sodium nitrite and hydrochloric acid, it yields a yellow diazo-derivative, which, when boiled with alcohol, yields the phenylethylmethylpyrazole previously obtained by Claisen and Meyerowitz. If water is used instead of alcohol, the corresponding hydroxypyrazole is obtained, melting at 104°. The diazo-derivative forms crystallisable colouring matters with phenols and amines.

C. H. B.

Carbonylorthamidophenol and Thiocarborthamidophenol. By S. Chelmicki (*J. pr. Chem.* [2], **42**, 440—445; compare Abstr., 1887, 477).—When carbonylorthamidophenol is heated with aniline in a sealed tube at 200—210°, and the product treated with sulphuric acid, decolorised by animal charcoal, and crystallised from alcohol, white, brittle needles of the formula $C_{13}H_{10}N_2O$ are obtained. This new substance melts, with decomposition, at 230°, and dissolves in most solvents except water; strong hydrochloric acid at 160° decomposes it into orthamidophenol hydrochloride, aniline hydrochloride, and carbonic anhydride; chloride of lime converts it, in acetic acid solution, into a chloro-derivative, $C_{13}H_8Cl_2N_2O$, melting at 276°. This substance is isomeric with Kalckhoff's anilidocarbamidophenol (Abstr., 1883, 1110), and must therefore be $C_6H_4{<}\substack{NH\\ O}{>}C{:}NPh$.

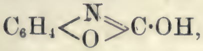
Nitrocarbonylorthamidophenol, [NH : O : NO_2 = 1 : 2 : 4], crystallises in long, yellow needles melting at 240—241° (uncorr.; Bender's nitranhydro-orthamidophenyl carbonate melts at 256°, Abstr., 1887, 38). When this compound is treated with potash, it is converted into nitrocatechol, [OH : OH : NO_2 = 1 : 2 : 4], melting at 170° (168°, according to Weselsky and Benedikt, Abstr., 1878, 575).

Orthohydroxyphenylallylthiocarbamide, $OH{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, is obtained by mixing allyl isothiocyanate (1 mol.) with orthamidophenol suspended in alcohol, and leaving the mixture at rest for some time. It forms white crystals which melt at 99°, and are more or less soluble in all the usual solvents. When it is heated with hydrochloric acid at 130°, it is converted into thiocarborthamidophenol.

Thiocarborthamidophenol evolves hydrogen sulphide when heated above its melting point; with ammonia at 200°, it is decomposed into carbamidophenol, carbonic anhydride, and ammonium sulphide. When an alcoholic solution of iodine is added to thiocarborthamidophenol dissolved in sodium hydroxide as long as the iodine is decolorised, crystals of the bisulphide $S_2(C\lessgtr^{N}_{O}>C_6H_4)_2$ (Abstr., 1887, 477) are formed; this substance melts at 110°, and dissolves in most solvents.

A. G. B.

Derivatives of Carbonylorthamidophenol and of Thiocarborthamidophenol. By P. Seidel (*J. pr. Chem.* [2], **42**, 445—457). —Kalckhoff's anilidocarbamidophenol is more easily obtained than Chelmicki's compound (preceding abstract); this is evidence that carbonylorthamidophenol is $C_6H_4<^{NH}_{-O}>CO$, for the doubly-linked oxygen atom might be expected to be more difficult to displace than the group —SH. The ethyl compound, $C_6H_4<^{NEt}_{-O}>CO$, cannot be made to react with aniline. The crystals of carbonylorthamidophenol soon lose their lustre in air, being changed to small needles; the author suggests that the unstable crystals are



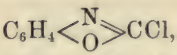
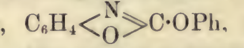
$$C_6H_4<^{N}_{O}\geqslant C{\cdot}OH,$$

and the stable crystals, $C_6H_4<^{NH}_{-O}>CO$. The crystals of thiocarborthamidophenol do not change, and this is in accord with the general belief that the stable form of this compound is $C_6H_4<^{N}_{O}\geqslant C{\cdot}SH$, a formula supported by the fact that by treatment of orthamidophenol with thiocarbonyl chloride, the same thiocarborthamidophenol is obtained as that obtained by the action of carbon bisulphide on carbonylorthamidophenol.

By the action of ethylorthamidophenol (m. p. 107·5°, not 167·5° as given by Förster, Abstr., 1880, 464) on thiocarbonyl chloride, a *thiocarbonylethylamidophenol* is obtained which melts at 112°, and boils undecomposed above 300°; it is different from Chelmicki's ethyl derivative (Abstr., 1887, 477). This compound is decomposed by strong hydrochloric acid at 170° into ethylorthamidophenolcarbonic anhydride and hydrogen sulphide, showing that its constitution is $C_6H_4<^{NEt}_{-O}>CS$. By heating this derivative with aniline and lead oxide, an anilide is, with some difficulty, obtained free from sulphur and homologous with Chelmicki's anilide (previous abstract); the difficulty with which it is obtained confirms the double linking of the sulphur to the carbon and, therefore, the above formula.

To obtain methylorthamidophenol, orthamidophenetoïl was methylated with methyl iodide in the cold, by which means the hydriodides of methylorthamidophenetoïl, dimethylorthamidophenetoïl, and orthamidophenetoïl, and *amidophenetoïltrimethylammonium iodide* were obtained. The last-mentioned crystallises in nacreous, violet-tinted leaflets, freely soluble in hot water. The mixture of the three methylorthamidophenetoïls was heated with strong hydrochloric acid at 170°, and the mixed methylorthamidophenols thus obtained were treated with thiocarbonyl chloride. This treatment yields *thiocarbonylmethylorthamidophenol* in colourless needles which melt at 128°, and boil undecomposed above 300°; strong hydrochloric acid at 170° decomposes it into methylorthamidophenol, carbonic anhydride, and hydrogen sulphide, so that its constitution is similar to that of thiocarbonylethylorthamidophenol (see above).

Methylorthamidophenol crystallises in colourless leaflets which soon oxidise and become brown in air; it melts with decomposition at 80°.

Carborthamidophenol chloride,  $C_6H_4{<}\substack{N\\O}{>}CCl$, is obtained when thiocarborthamidophenol and phosphoric chloride are mixed together and the product distilled; thiophosphoryl chloride passes over below 130°, and the portion that distils between 130° and 205° separates after a time into crystals and an oil; the crystals were not investigated. The oil is carborthamidophenol chloride; it boils at 201—202°, solidifies in a freezing mixture, and melts at 7°; it is a feeble base forming a well-crystallised nitrate and hydrochloride; it is decomposed by water into carborthamidophenol and hydrochloric acid. With phenol, it yields two compounds, one of which is a *carborthamidophenol phenyl ether*,  $C_6H_4{<}\substack{N\\O}{>}C{\cdot}OPh$, melting at 56° and boiling at 310°, whilst the other melts at 190° and boils at a much higher temperature. With aniline, carborthamidophenol chloride yields Kalckhoff's anilide. Carborthamidophenol chloride is also produced when methyl and ethyl thiocarbonylorthamidophenols are heated with phosphoric chloride. A. G. B.

Preparation of Anhydrous Diazo-salts. By E. KNOEVENAGEL (*Ber.*, **23**, 2994—2998).—Up to the present time very few diazo-salts have been obtained in the anhydrous condition, the most important exceptions being diazobenzene sulphate and nitrate. The author finds that all the salts may be readily prepared in the anhydrous condition by treating the amido-compound in acid alcoholic solution with amyl nitrite. To prepare diazobenzene sulphate by this method, 15 grams of aniline is dissolved in 9—10 parts of absolute, or at least 95 per cent. alcohol, and 20 grams of concentrated sulphuric acid carefully added; aniline sulphate separates at first, but redissolves on adding the remainder of the acid. When cold, 20 grams of amyl nitrite are added, and the mixture well cooled, ice being preferably employed in the preparation of large quantities. After 10—15 minutes, diazobenzene sulphate usually separates in beautiful needles, the whole mass solidifying to a crystalline magma, which, on filtering and washing with alcohol and ether, yields the compound in an almost pure condition. If the sulphate does not separate after 10—15 minutes, the addition of a few drops of ether causes an immediate crystallisation, and a further quantity of the salt may be obtained by adding ether to the mother liquor. The diazobenzene sulphate thus obtained has all the properties assigned to it by Griess, and is more readily prepared in this manner than by his method.

Diazobenzene nitrate is most readily prepared by adding rather more than the theoretical quantity of amyl nitrite to a cold saturated alcoholic solution of aniline nitrate containing a little free nitric acid, cooling well with ice. On the addition of a small quantity of ether, diazobenzene nitrate separates in beautiful needles, which explode, when dry, very violently, either on heating or by percussion.

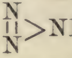
Diazobenzene chloride, which has hitherto not been obtained in the solid condition, is easily prepared in a similar manner to the nitrate; very careful cooling is necessary on adding the amyl nitrite, as the diazotisation of aniline chloride proceeds very rapidly. After a short time, the salt separates in almost colourless needles, which are collected, washed with a little alcohol and ether, and dried over sulphuric acid in a vacuum. The yield is almost quantitative; the determination of chlorine and nitrogen gave numbers agreeing closely with the formula $C_6H_5{\cdot}N_2Cl$. Diazobenzene chloride decomposes on heating with a slight explosion, but only gives a slight detonation by percussion. It is soluble in alcohol, but insoluble in ether, benzene, and light petroleum; water dissolves it with great avidity, and it deliquesces in moist air, undergoing considerable decomposition, but is fairly stable in dry air, especially in the dark.

The following diazo-compounds have also been obtained in the anhydrous condition by this method:—The *diazo-sulphates* of orthotoluidine, paratoluidine, paraphenetidine, paranisidine, and metanitraniline; the *diazo-nitrates* of ortho- and para-toluidine; the *diazo-chlorides* of paratoluidine, paraphenetidine, and paranisidine.

H. G. C.

Action of Alkalis on Acid Salts of Diazobenzene: Ethyl Diazobenzoate. By T. CURTIUS (*Ber.*, **23**, 3033—3036).—By heating diazobenzene sulphate with the calculated quantity of barium hydroxide and extracting with ether, a very volatile, feebly basic compound is obtained which is volatile with steam, melts at $-3°$, and has an odour resembling that of rose water; although no evolution of nitrogen could be detected, analysis shows that only 2 atoms of nitrogen are combined with 3 benzene nuclei. A corresponding compound may be prepared in the same manner from ethyl metadiazobenzoate sulphate. No hydrazine could be detected in the mother liquors, and only in one experiment, with aluminium and alkalis, was any formed by the reduction of the compound in either acid or alkaline solutions. Attempts to prepare diazobenzene, by the action of silver nitrite on dry aniline hydrochloride dissolved in some indifferent medium, were unsuccessful, diazoamidobenzene being the sole product, and, in a similar manner, ethyl metamidobenzoate yields ethyl diazoamidobenzoate. Diazoamidobenzene may be prepared by mixing very dilute, cold, aqueous solutions of aniline hydrochloride and sodium nitrite; after washing with cold water, the product is quite pure. The potassium and silver salts of diazobenzene, prepared according to the method described by Griess, were found on analysis to contain only two-thirds the theoretical quantity of nitrogen, the proportion being 6 atoms of carbon to 1 of nitrogen. The quantity of metal present agreed closely with the theory. The author is unable to assign any formula to these compounds.

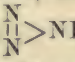
J. B. T.

Hydrogen Nitride (Azoimide). By T. CURTIUS (*Ber.*, **23**, 3023—3033).—*Hydrogen nitride*,  $\left.\begin{array}{c}N\\ \|\\ N\end{array}\right>NH$, is formed, under certain conditions, by the action of sodium nitrite on hydrazine hydrochloride; the reaction is strictly analogous to the formation of nitrogen from ammonium chloride and sodium nitrite. To obtain it in this manner is, however, a matter of considerable difficulty, and it is best prepared from *hippurylhydrazine* in the manner described below.

Benzoylhydrazine, $NH_2{\cdot}NHBz$, is formed on mixing molecular proportions of ethyl benzoylglycollate and hydrazine hydrate; it crystallises from alcohol in large, lustrous plates, melts at 112°, reduces alkaline copper solution in the cold, and dissolves in cold water, but is only sparingly soluble in ether. It is not changed on boiling with water, but is hydrolysed by the action of dilute alkalis. The same compound is also obtained by the action of hydrazine hydrate on ethyl benzoate.

Benzoylbenzalhydrazine, $NHBz{\cdot}N{:}CHPh$, is prepared by adding benzaldehyde to benzoylhydrazine in molecular proportion, and is deposited from alcohol in long, colourless crystals which melt at 203°, are very sparingly soluble in ether, and insoluble in water.

Symmetrical dibenzoylhydrazine, $NHBz{\cdot}NHBz$, is obtained by boiling benzoylhydrazine; it crystallises from alcohol in silky needles melting at 233°, and is hydrolysed by treatment with acids or alkalis.

On heating a cold aqueous solution of benzoylhydrazine with an equal molecular proportion of sodium nitrite, and acidifying with acetic acid, *benzoylazimide* (*benzoic nitride*),  $\left.\begin{array}{c}N\\ \|\\ N\end{array}\right>NBz$, separates as an oily liquid which solidifies after some time. It crystallises in colourless prisms which melt at 29—30°, explodes on heating, and is volatile with steam. By treatment with alkalis, it is hydrolysed, but undergoes no change on boiling with acids; it reduces ammoniacal silver solution, but has no action on alkaline copper solution; it has a powerful odour resembling that of benzoic chloride, and rapidly attacks the skin.

Hydrazinacetic acid (amidoglycocine), $NH_2{\cdot}NH{\cdot}CH_2{\cdot}COOH$, is prepared by acting with ethyl benzoylglycollate (1 mol.) on hydrazine hydrate (2 mols.); the benzoylhydrazine which first separates is removed, and after some time the acetic acid derivative is deposited from the mother liquor; it is purified by repeated recrystallisation from alcohol, and forms large, lustrous plates, which melt at 93°, and are insoluble in ether. It has a sweet taste, gives with alkaline copper solution a deep violet colour, and, on warming, a precipitate of cuprous oxide. A red colour is produced with neutral ferric chloride solution, and ammoniacal solution of silver is reduced in the cold. The compound is hydrolysed by warming with acids or alkalis. *Benzalhydrazineacetic acid*, $CHPh{:}N{\cdot}NH{\cdot}CH_2{\cdot}COOH$, is formed by the action of benzaldehyde on the previous compound, and crystallises from alcohol in silky, lustrous needles melting at 156·5°. *Hippurylbenzalhydrazine*,

$NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$, is prepared by adding the calculated quantity of hydrazine hydrate to an alcoholic solution of ethyl hippurate; it crystallises from alcohol in colourless, lustrous needles which melt at 162·5, and are sparingly soluble in ether; the yield is 90 per cent. The compound reduces ammoniacal silver solution in the cold; with alkaline copper solution, a green colour is produced, and after some time reduction occurs. *Hippurylbenzalhydrazine*,

$$NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CHPh,$$

is formed by the action of benzaldehyde on the previous compound, and crystallises from alcohol in lustrous plates which melt at 182°. By the action of acetic acid and sodium nitrite at 0° on an aqueous solution of hippurylhydrazine, a compound is obtained crystallising from alcohol in colourless needles which melt at 98°; it is probably either *nitrosohippurylhydrazine*, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}N(NO){\cdot}NH_2$, or *nitrosohydrazine hippuric acid*, $NO{\cdot}NH{\cdot}N{:}CPh{\cdot}NH{\cdot}CH_2{\cdot}COOH$; by treatment with acids or alkalis, azoimide and hippuric acid are formed; on boiling with water, an indifferent gas is produced, together with a very insoluble substance that has not yet been investigated. The nitroso-compound readily dissolves in alkalis or ammonia, and the solution exhibits a beautiful blue fluorescence. On adding silver nitrate to the ammoniacal solution, a white, explosive, silver salt is precipitated.

Azoimide may be obtained from benzoylhydrazine or hydrazine-acetic acid, but is best prepared from the hippuryl compound by dissolving it in dilute soda, and decomposing the boiling solution with dilute sulphuric acid; the azoimide distils over with the steam, and is passed into neutral silver nitrate solution, the precipitated silver salt is collected, washed with water, dried at 60—70°, and treated with dilute sulphuric acid. By repeating this process, a solution is obtained containing 27 per cent. of azoimide; on bringing the solution into contact with ammonia, thick, white vapours of the ammonium salt are formed. Azoimide itself is a gas, having a particularly nauseous odour, and resembling hydrogen chloride in its general properties. It is very soluble in water, and on distillation a concentrated solution passes over; the distillate gradually becomes weaker until equilibrium is established, a solution of definite strength being obtained which boils constantly. A piece of blue litmus paper held over the solution turns red. Iron, zinc, copper, aluminium, and magnesium readily dissolve in a 7 per cent. solution of the gas, hydrogen being evolved. Gold and silver also appear to be attacked. Azoinide is liberated by the action of dilute sulphuric acid on any of the salts; with concentrated sulphuric acid, the azoimide is itself decomposed, *Barium nitride*, N_6Ba, is obtained in lustrous, hard crystals which are readily soluble in water, and explode with a green flash on heating. *Silver nitride*, N_3Ag, crystallises in prisms which melt at about 250° with a violent explosion.

J. B. T.

Action of Acid Chlorides on Acid Amides. By A. PICTET (*Ber.*, **23**, 3011—3016).—Benzanilide and acetic chloride are formed on heating benzoic chloride and acetanilide at 140°; the same result is obtained if the compounds are dissolved in toluene. This reaction is found to be a general one, both for the aromatic and fatty amides and chlorides; and the author explains it by assuming that an additive compound is first formed which then decomposes, the radicles containing the least number of carbon atoms combining with the chlorine, whilst the higher carbon derivatives unite with the amide complex. The production of benzanilide, for example, would be preceded by the formation of the hypothetical compound acetobenzanilide hydrochloride, NHPhBzAcCl. These observations confirm those of Paal and Otten (compare Abstr., 1890, 1415). J. B. T.

Action of Sodium on Acid Amides. By T. Curtius (*Ber.*, **23**, 3037—3041).—*Sodium benzamide*, COPh·NHNa or ONa·CPh:NH, is prepared by boiling a benzene solution of benzamide with rather less than the calculated quantity of sodium. The operation takes about 30 hours, the precipitated salt is separated, treated repeatedly with ether in an extraction apparatus, and dried over sulphuric acid and quicklime. It is a white, crystalline powder, insoluble in ether, chloroform, or benzene; it is very readily decomposed by water, or by dissolving in alcohol, but is not hygroscopic, and on distillation, yields benzene, soda, ammonia, and a little benzonitrile.

Sodium dibenzamide, NBz_2Na, is obtained by dissolving dibenzamide in xylene, and boiling the solution for 30 hours with a slight excess of sodium; no evolution of ammonia occurs; the product crystallises from ether in small, white, lustrous plates which melt at 150° and resolidify on heating to 230°, and then do not melt at 300°. The solid is readily soluble in water. On distillation, sodium dibenzamide yields only traces of benzene; it is much more stable than the benzamide salt, and a recently prepared aqueous solution gives precipitates with the salts of many of the heavy metals.

By the action of sodium on acetamide, considerable quantities of ammonia are evolved, and a viscid liquid separates, which after some time becomes crystalline; it contains nitrogen, and is possibly *sodium diacetamide*, NAc_2Na.

By the action of iodine on finely divided sodium benzamide, or sodium dibenzamide suspended in ether, additive compounds are formed which readily crystallise, but do not show a constant composition. Benzamide and iodine give the compound $NH_2BzI{\cdot}NH_2BzI$ (?), crystallising in long, slender, olive-green prisms, which exhibit pleochroism and melt at 110—112° without decomposition. The compound is stable in air, and insoluble in water, but readily dissolves in glacial acetic acid; on shaking with mercury, benzamide and mercuric iodide are formed, whilst by distillation, or on boiling with water or alcohol, it is decomposed into iodine and benzamide. Iodine and dibenzamide give a compound, $NH_4Bz_2I_2$, which crystallises in large, green prisms melting at 118—120°; it is readily soluble in chloroform, and resembles the preceding substance in properties.

Tribenzamide, NBz_3, is formed together with dibenzamide by treating benzamide with excess of benzoic chloride; it is very sparingly soluble in alcohol, and is deposited in silky, lustrous needles which melt at 202°, sublime without decomposition, and yield benzoic acid and ammonia when boiled with soda. J. B. T.

α-**Toluamide and its Derivatives.** By A. Purgotti (*Gazzetta*, **20**, 172—178).—When benzonitrile is treated with concentrated sulphuric acid (sp. gr. = 1·82), an energetic reaction takes place, and *α-toluamide* (phenylacetamide) is formed. An almost theoretical yield is obtained if the proportion of the acid used contains the quantity of water theoretically necessary for the transformation.

Chloralphenylacetamide, prepared by heating a mixture of anhydrous chloral and phenylacetamide in molecular proportion for half an hour, crystallises from alcohol in minute, nacreous scales which melt at 145°, and dissolve in alcohol and in boiling ether and benzene.

Phenylacetylhydrazine, $CH_2Ph·CO·NH·NHPh$. — Phenylacetamide reacts with phenylhydrazine like formamide, acetamide, &c., according to Justus' equation $R·CONH_2 + NH_2·NHPh = R·CONH·NHPh + NH_3$. A mixture of the amide and phenylhydrazine in molecular proportion is heated at 120—130°; the product crystallises from alcohol in colourless scales which melt at 175—176°, and are moderately soluble in warm alcohol.

When phenylacetamide is heated with aniline in molecular proportion, at about 150°, ammonia is evolved, and the product, after repeated precipitation with water and recrystallisation from alcohol, yields nacreous scales which melt at 116—117°, and are readily soluble in alcohol. This compound seems to be identical with Hofmann's *α*-toluylanilide.

Phenylacetylparatoluidide is obtained by heating the amide with paratoluidine at 160—180° until the evolution of ammonia ceases. It crystallises in small, transparent tables which melt at 135—136°, and dissolve readily in alcohol and ether. S. B. A. A.

Conversion of Nitriles into Imido-ethers. By A. Pinner (*Ber.*, **23**, 2917—2919).—It has been shown that imido-ethers are formed by the action of hydrogen chloride on a mixture of an alcohol and a nitrile. Further experiments have shown, however, that certain aromatic nitriles, in which a carbon atom, in the ortho-position relative to the CN group, is linked to another carbon atom, are incapable of forming imido-ethers. It is also found that orthodicyanides only form monimido-ethers. The first of these conclusions is formed from a study of orthocyanotoluene, paracyanotoluene, paracyanoxylene, *α*-cyanonaphthalene, and metacyano-xylene [Me : Me : CN = 1 : 3 : 4], whilst the second is deduced from the investigation of metadicyanotoluene [Me : CH : CN = 1 : 3 : 4]. J. B. T.

Diphenyloxycyanidine. By A. Pinner (*Ber.*, **23**, 2919—2922; compare Abstr., 1890, 496).—*Ethyl benzamidylcarbamate*,

$$NH{:}CPh·NH·COOEt,$$

is prepared by the action of aqueous soda and ethyl chlorocarbonate on benzamidine hydrochloride; it crystallises from alcohol in thick, white prisms which melt at 57—58°, and are almost insoluble in water. On heating the compound to about 150°, decomposition takes place, alcohol and ethyl carbamate are eliminated, and diphenyloxycyanidine (m. p. 289°) is formed. By the action of alcoholic ammonia on the latter substance, it is converted into benzamidine and ethyl carbamate, whilst with aqueous ammonia, benzamide and urethane are formed.

Dibenzamidylcarbamide, $CO(NH\cdot CPh{:}NH)_2$, is obtained by the action of carbonyl chloride on benzamidine; diphenyloxycyanidine is also produced during the reaction, and the two compounds cannot be completely separated; it crystallises from alcohol in prisms which are soluble in soda, and melt at 229° with evolution of ammonia. The compound is completely converted into diphenylcyanidine on heating above its melting point. Experiments with propionamidine were unsuccessful. By the action of carbonyl chloride on capronamidine *dicapronamidinebiuret*, $NH(CO\cdot NH\cdot C_6H_{11}{:}NH)_2$, is obtained, crystallising from alcohol in stellate groups of slender, white needles melting at 236°. J. B. T.

Amidines. By A. PINNER (*Ber.*, **23**, 2923—2927; compare Abstr., 1889, 1004).—*Ethenyldiphenylureïd*, $NHPh\cdot CO\cdot N{:}CMe\cdot NH\cdot CO\cdot NHPh$, is formed by the action of phenyl cyanate on acetamidine; it crystallises from acetone in small, slender needles, melts at 169°, and yields acetylphenylcarbamide on boiling with 6—8 parts of 50 per cent. acetic acid solution.

Propenyldiphenylureïd, $NHPh\cdot CO\cdot N{:}CEt\cdot NH\cdot CO\cdot NHPh$, is prepared from propionamidine in a similar manner to the ethenyl derivatives, and crystallises from acetone in slender, white needles melting at 169—170°. On distillation, it yields diphenylcarbamide, whilst on boiling with dilute acetic acid, propionylphenylcarbamide is formed.

Action of Aldehydes on Benzamidine.—Further investigation renders it probable that the compound obtained by the action of benzaldehyde on benzamidine (*loc. cit.*) is *diphenyl dicyanide*, $C_{14}H_{10}N_2$, and not benzylidenebenzamidine, $C_{14}H_{12}N_2$, as stated. Lophine is also formed in a very small quantity during the reaction. A yellow, amorphous product of the formula $C_{13}H_{18}N_2O_2$ is obtained by the action of acetaldehyde on benzamidine; it melts below 100°, is soluble in alcohol, ether, and chloroform, but insoluble in water or light petroleum. It yields an amorphous *platinochloride*, which melts at about 108°. On heating the base at 130°, and treating the product with hydrochloric acid and platinum chloride solution, an amorphous *platinochloride* is formed which melts at 183° with decomposition, and is probably a purer preparation of the above lower melting compound. J. B. T.

Action of Benzamidine on the Ethereal Salts of Aromatic Orthohydroxy-acids. By A. PINNER (*Ber.*, **23**, 2934—2941).—By the action of sodium hydroxide (2 mols.) on ethyl salicylate and benzamidine hydrochloride, crystals are obtained from which *benzamidine salicylate* may be separated by treatment with acetone; it is deposited in large prisms which melt at 202°, and are readily soluble in water or alcohol. The residue remaining after the extraction with acetone forms slender, yellow needles melting at 246°. It is insoluble in organic media or in aqueous soda, and gives a red colour with concentrated sulphuric acid. The same compound may be prepared in larger quantity by heating an ethereal solution of benzamidine with ethyl salicylate at 40° for 10—12 hours; the ether is evaporated, and the residue boiled out with water. The substance has the formula $C_{21}H_{15}N_3O$, and is formed by the elimination of water, alcohol, and ammonia from 1 mol. of ethyl salicylate and 2 mols. of benzamidine. The *acetyl* compound, $C_{21}H_{14}N_3O{\cdot}Ac$, is prepared by treatment with acetic anhydride and zinc chloride, and crystallises from alcohol in colourless, lustrous prisms melting at 140—141°.

On adding hydrochloric acid to the alkaline filtrate obtained after the separation of the benzamidine salicylate, *benzamide salicylate* is precipitated; it crystallises from hot water in silky, lustrous plates which melt at 120°. The compound had been previously prepared (compare Abstr., 1889, 1004), but its constitution was unknown.

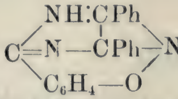
By the action of benzamidine on the methyl salts of the hydroxytoluic acids, compounds are obtained corresponding in properties and constitution to the above salicylic acid product. The derivative of orthohydroxytoluic acid [COOH : OH : Me = 1 : 2 : 3] melts at 214°; that of metahydroxytoluic acid [1 : 2 : 4], at 235°; whilst the product from parahydroxytoluic acid [1 : 2 : 5] melts at 202°. All these compounds are insoluble in acids and alkalis, and are exceedingly difficult to burn. Paradihydroxybenzoic acid [COOH : OH : OH = 1 : 2 : 5] also condenses with benzamidine; the compound is deposited from benzene in small, nodular crystals, melting at 265—266°, with previous softening at 250°.

The formation of the above compounds probably takes place in two stages; in the case of salicylic acid, the hypothetical intermediate product has one or other of the formulæ

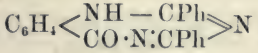
$NH{:}CPh{\cdot}NH{\cdot}C(C_6H_4{\cdot}OH){:}N{\cdot}CPh{:}NH$ or

$$C_6H_4<\begin{array}{l}NH{\cdot}CPh{:}NH\\CO{\cdot}NH{\cdot}CPh{:}NH\end{array};$$

ammonia is then eliminated, the constitution of the final product being represented by the formulæ



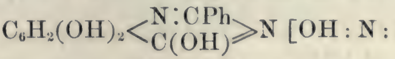
and



$$C_6H_4<\begin{array}{l}NH-CPh\\CO{\cdot}N{:}CPh\end{array}>N$$

respectively.

On heating ethylphloroglucinoltricarboxylic acid with benzamidine for two hours at 130°, 2 mols. of carbonic anhydride are eliminated, and a compound is formed to which the formula



$$C_6H_2(OH)_2<\begin{array}{l}N{:}CPh\\C(OH)\end{array}>N\ [OH : N : C = 1 : 2 : 3]$$

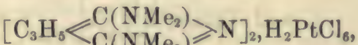
is given. J. B. T.

Imido-ethers. By A. PINNER (*Ber.*, **23**, 2942—2956).—IMIDO-ETHERS FROM TRIMETHYLENE CYANIDE.—Trimethylene cyanide is prepared by mixing trimethylene bromide with 2·5 parts of 85 per cent. alcohol, and adding $\frac{2}{3}$ part of finely divided potassium cyanide; after boiling for 5—6 hours, the product is filtered, the greater part of the alcohol removed, the residue dissolved in water, and extracted with ether; after distilling off the ether, the crude product is fractionated; the yield is 85 per cent. of theory. The *hydrochlorides* of *glutaramidyl ethyl ether* and *glutaramidyl methyl ether* are unstable. *Glutar-*

amidyl isobutyl ether hydrochloride, $C_3H_6[C(NH)\cdot O\cdot CH_2\cdot CHMe_2,HCl]_2$, is readily soluble in water or alcohol and crystallises in plates. By the action of water, ammonia is eliminated, and *isobutyl glutarate*, $C_3H_6(COO\cdot CH_2\cdot CHMe_2)_2$, is formed; it is a viscid liquid boiling at 270°. On heating the imido-ether hydrochloride, it softens at 110°, and at higher temperatures decomposes into glutarimide, isobutyl chloride, and isobutylamine hydrochloride. By the action of aqueous ammonia, it is converted into *glutaramide*, $C_3H_6(CO\cdot NH_2)_2$, which is soluble in water or alcohol, and melts at 176° with evolution of ammonia. On treatment with alcoholic ammonia, isobutyl alcohol and ammonium chloride are eliminated, and an additive compound is formed consisting of the hydrochlorides of glutaramidine and glutarimidine in molecular proportion; on dissolving it in water, the imidine is formed, but it could not be isolated on account of its great solubility. On evaporating the mother liquor from the above additive compound, large rhombic crystals of *glutaramidine hydrochloride*, $C_3H_6[C(NH)NH_2,HCl]_2 + 2H_2O$, are obtained, which are readily soluble in water or alcohol but cannot be recrystallised; the hydrated salt melts at 79°, and the anhydrous compound at 189°. The *platinochloride* is deposited in flat, yellow prisms which melt at 214° with decomposition. *Glutarimidyl acetate*, $C_3H_6[C(NH)OAc]_2$, is prepared by the action of acetic anhydride and sodium acetate on glutaramidine hydrochloride, and crystallises in small, lustrous needles melting at 210—211°.

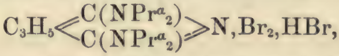
By the action of primary amines on the hydrochlorides of glutarimido-ethers, substituted glutarimidines are formed, the hydrochlorides and platinochlorides of which are excessively unstable. *Diethylglutarimidine platinochloride* $(C_5H_7N_3Et_2)_2,H_2PtCl_6$, is obtained in yellowish-red crystals which melt at 179°. Secondary amines yield tetra-substituted glutarimidines; neither the free bases nor the hydrochlorides could be obtained in a pure state.

Tetramethylglutarimidine platinochloride,



$$[C_3H_5<\begin{matrix}C(NMe_2)\\C(NMe_2)\end{matrix}>N]_2,H_2PtCl_6,$$

is deposited in dark-red, cubical crystals which darken at 190°, and melt at 210° with decomposition. The corresponding *tetrethyl* compound crystallises in long, dark red needles, melting at 141°. The *tetrapropyl* derivative forms reddish-yellow crystals melting at 178°. *Dibromotetrapropylglutarimidine hydrobromide*,



$$C_3H_5<\begin{matrix}C(NPr^a{}_2)\\C(NPr^a{}_2)\end{matrix}>N,Br_2,HBr,$$

is prepared by the action of bromine on the hydrochloride, and crystallises in long, reddish-yellow needles which melt at 86°, and are very sparingly soluble in water.

IMIDO-ETHERS OF HYDROXYPROPIONITRILE AND PHENYLHYDROXYACETONITRILE.—The *methyl* and *ethyl* ethers of hydroxypropimide are very unstable; the *hydrochloride* of the *propyl ether*,

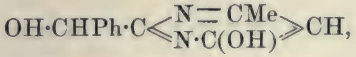
$$OH\cdot CHMe\cdot C(NH)OPr^a,HCl,$$

forms long, colourless needles which melt at 68—69° with decomposition. The corresponding *amyl* derivative is deposited in slender needles melting at 69°. By the action of alcoholic ammonia, *hydroxypropamidine hydrochloride*, $OH\cdot CHMe\cdot C(NH)\cdot NH_2,HCl$, is formed, crystallising from alcohol in flat needles which melt at 171°. The *nitrate* softens at 78°, and melts at 84°.

Dimethyllactamidine hydrochloride, $OH\cdot CHMe\cdot C(NMe)\cdot NHMe,HCl$, is prepared by the action of methylamine on the imido-amyl ether, and is deposited in colourless, rhombic crystals, melting at 215°. Attempts to prepare an asymmetrical dimethyl derivative by the action of dimethylamine were unsuccessful.

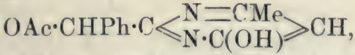
Diacetylphenyllactamidine, $OAc\cdot CHPh\cdot C(NH)\cdot NHAc$, is obtained on treating phenylhydroxyacetamidine with acetic anhydride and sodium acetate, and melts at 210°.

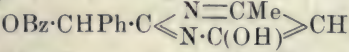
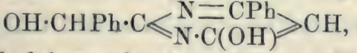
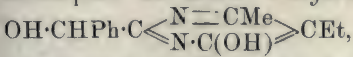
Hydroxybenzylmethylhydroxypyrimidine,



$$\mathrm{OH{\cdot}CHPh{\cdot}C}\Big<\substack{\mathrm{N{=}CMe}\\ \mathrm{N{\cdot}C(OH)}}\Big>\mathrm{CH},$$

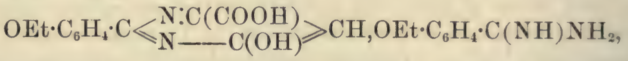
is formed on mixing phenylhydroxyacetamidine, ethyl acetoacetate, and sodium hydroxide in molecular proportion; it crystallises from amyl alcohol in long needles which melt at 216°, and are sparingly soluble in water, alcohol, ether, or benzene, but readily dissolve in dilute alcohol, alkalis, and acids. The *hydrochloride* crystallises in needles melting at 217° with previous softening at 212°. The *picrate* forms slender, yellow needles melting at 175°. The *silver* salt is white and sparingly soluble.

The *acetyl* derivative,  $\mathrm{OAc{\cdot}CHPh{\cdot}C}\Big<\substack{\mathrm{N{=}CMe}\\ \mathrm{N{\cdot}C(OH)}}\Big>\mathrm{CH}$, is formed by the action of acetic anhydride; it melts at 170°, and yields a white, amorphous *silver* salt. The *picrate* forms slender, yellow needles which melt at 160° with decomposition; the *hydrochloride* melts at 188°.

The *benzoyl* derivative,  $\mathrm{OBz{\cdot}CHPh{\cdot}C}\Big<\substack{\mathrm{N{=}CMe}\\ \mathrm{N{\cdot}C(OH)}}\Big>\mathrm{CH}$, is formed by the action of benzoic chloride on the pyrimidine, and melts at 205—208°. The *hydrochloride* crystallises from glacial acetic acid in stellate groups of small needles melting at 240°. *Hydroxybenzylphenylhydroxypyrimidine*,  $\mathrm{OH{\cdot}CHPh{\cdot}C}\Big<\substack{\mathrm{N{=}CPh}\\ \mathrm{N{\cdot}C(OH)}}\Big>\mathrm{CH}$, is prepared from the amidine and ethyl benzoylacetate; it crystallises in fine needles which melt at 218°, with previous softening at 212°. *Hydroxybenzyldimethylhydroxypyrimidine* is formed from ethyl methylacetoacetate and melts at 155°. It yields a white, amorphous *silver salt*. The *acetate* crystallises in stellate groups of lustrous needles, which decompose at 100°. *Hydroxybenzylmethylethylhydroxypyrimidine*,  $\mathrm{OH{\cdot}CHPh{\cdot}C}\Big<\substack{\mathrm{N{=}CMe}\\ \mathrm{N{\cdot}C(OH)}}\Big>\mathrm{CEt}$, from ethyl ethylacetoacetate, crystallises in small needles which melt at 148—152°.

IMIDO-ETHERS FROM ORTHO- AND PARA-ETHOXYBENZONITRILE.—*Orthoethoxybenzonitrile*, $OEt\cdot C_6H_4\cdot CN$, is a yellow, viscid, bitter liquid, which boils at 258°, is volatile with steam, and miscible with alcohol, ether, or light petroleum. The preparation of the pure imido-ether is a matter of some difficulty; the nitrile is therefore treated with alcohol and hydrogen chloride. and the product converted into *ortho-ethoxybenzamidine hydrochloride*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C(NH){\cdot}NH_2,HCl}$, by the action of alcoholic ammonia; it is deposited in short, colourless, hexagonal crystals melting at 218°. *Ortho-ethoxyphenylmethylhydroxypyrimidine*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N=CMe}}{\mathrm{N{\cdot}C(OH)}}{>}\mathrm{CH}$, is formed from the amidine and ethyl acetoacetate, and melts at 146°.

Para-ethoxybenzonitrile is deposited in long, yellow, rhombic crystals which melt at 69°, boil at 258°, and resemble the ortho-compound in properties; the preparation was not quite pure. *Para-ethoxybenzimidoethyl ether hydrochloride*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C(NH){\cdot}OEt,HCl}$, crystallises in white needles which decompose on heating into ethyl chloride and *para-ethoxybenzamide*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2}$; this same compound is also formed by the action of soda on the amidine hydrochloride, and is deposited in long crystals melting at 206°. *Para-ethoxybenzamidine hydrochloride*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C(NH){\cdot}NH_2.HCl}$, is prepared by the action of alcoholic ammonia on the crude imido-ether, and is deposited from alcohol in long, hexagonal crystals melting at 260°. On treating the free base with ethyl acetoacetate, *para-ethoxyphenylmethylhydroxypyrimidine*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{NC=Me}}{\mathrm{N{\cdot}C(OH)}}{>}\mathrm{CH}$, is obtained, crystallising from alcohol in short, white prisms which melt at 204°. The same compound is formed by the action of ethyl acetomalonate on the amidine, carbonic anhydride being eliminated. *Para-ethoxyphenyldimethylhydroxypyrimidine*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N=CMe}}{\mathrm{N{\cdot}C(OH)}}{>}\mathrm{CMe}$, is prepared from ethyl methylacetoacetate, and crystallises from alcohol in small prisms melting at 216°. Ethyl ethylacetoacetate yields the corresponding ethylmethyl derivative, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N=CMe}}{\mathrm{N{\cdot}C(OH)}}{>}\mathrm{CEt}$, crystallising from alcohol in long needles which melt at 194°. *Para-ethoxyphenylmethylbenzylhydroxypyrimidine*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N=CMe}}{\mathrm{N{\cdot}C(OH)}}{>}\mathrm{C{\cdot}C_7H_7}$, is formed from ethyl benzylacetoacetate, and crystallises from alcohol, in which it is very soluble, in lustrous needles melting at 242°. *Para-ethoxydiphenylhydroxypyrimidine*, $\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N=CPh}}{\mathrm{N{\cdot}C(OH)}}{>}\mathrm{CH}$, from ethyl benzoylacetate, crystallises from alcohol in broad needles which melt at 2,4°. *Para-ethoxybenzamidine para-ethoxyphenylhydroxypyrimidinecarboxylate*,



$$\mathrm{OEt{\cdot}C_6H_4{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{N{:}C(COOH)}}{\mathrm{N{-\!\!-}C(OH)}}{>}\mathrm{CH,OEt{\cdot}C_6H_4{\cdot}C(NH)NH_2},$$

is formed by the action of ethyl oxylate on the amidine, and is deposited from alcohol in long, white, lustrous crystals melting at 280°, with previous softening at 275°. The *free acid* crystallises from alcohol in short needles which melt at 248° with decomposition.

J. B. T.

Compounds containing the Group $C_2N_2O_2$. By A. F. HOLLEMAN (*Ber.*, **23**, 2998—3001).—In the hope of obtaining compounds related to the dinitrosacyls (Abstr., 1889, 50), the author has examined the action of benzoic chloride on mercuric fulminate. The results are, however, not so simple as was expected, two crystalline compounds of quite a different constitution being formed. Mercuric fulminate, obtained according to de Bruyn's method (*Ber.*, **19**, 1370), and well washed with water, alcohol, and ether, was allowed to remain quietly in a cool place with an equal weight of benzoic chloride for 5—7 days; after that time, the fulminate had disappeared, and was replaced by a hard, greyish-white mass. On adding water to the latter, carbonic anhydride is evolved, and mercuric chloride passes into solution. The insoluble matter, after washing with cold water, is extracted with hot water, which takes up a white, crystalline compound, free from mercury, but containing nitrogen and melting at 107°. The residue is for the most part soluble in acetic acid, and crystallises out on cooling in beautiful needles which melt at 197°, and have the composition $C_{15}H_{12}N_2O_3$, as shown by the results of the analysis and molecular weight determination by Raoult's method. On boiling with alkalis, it is converted into benzoic acid, ammonia, and carbonic anhydride, and it is therefore probably *dibenzoylcarbamide*, but whether it is the symmetrical or asymmetrical compound has not yet been proved. The compound melting at 107° is also being more closely investigated, and it is hoped that the formation of these substances may throw some light on the constitution of fulminic acid.

By the action of benzoic chloride on potassium fulminate, a compound was obtained which also melts at 197°, but is not identical with dibenzoylcarbamide. It appears to be a mixed anhydride of benzoic and fulminuric acids. H. G. C.

Compounds of Phthalimide with Phenols. By O. OSTERSETZER (*Monatsh.*, **11**, 424—428).—The author has prepared the so called "resorcinolphthalimidesulphonic acid" of Reese (German Patent No. 44,268, 1887) by the action of sulphuric acid on a mixture of phthalimide (1 mol.) and resorcinol (2 mols.). The compound has the formula $C_{20}H_{13}O_7NS$, but does appear to be a sulphonic acid. It yields a sodium derivative, $C_{20}H_{12}NO_7SNa + 7H_2O$, which, when precipitated from its aqueous solution by means of alcohol, forms dark-coloured crystals; and a diacetyl compound, $C_{20}H_{11}O_7NSAc_2$, which is soluble in alcohol and chloroform, and may be obtained as a yellowish-green, crystalline powder, by cooling a saturated solution in acetic acid.

G. T. M.

Dihydrobenzaldehyde. By A. EICHENGRÜN and A. EINHORN (*Ber.*, **23**, 2870—2887; compare Abstr., 1887, 741).—The compound formed by the action of alkaline carbonates on the salts of anhydroecgonine dibromide proves not to be the analogue of orthobromocinnamene, as stated, but is a mixture of methyl tetrahydropyridylacetylene and dihydrobenzaldehyde; the small quantity of bromine previously found is due to the presence of unaltered anhydroecgonine dibromide. Methylamine is also formed in some quantity during the reaction.

Dibromanhydroecgonine dibromide hydrobromide,

$$C_5NH_7Me{\cdot}CHBr{\cdot}CHBr{\cdot}COOH,HBr,Br_2\ [Me : CH = 1 : 2],$$

is prepared by heating anhydroecgonine hydrochloride with 2 parts of bromine on the water-bath for 3—4 hours. It crystallises in well-developed, red, rhombic prisms, which melt at 145° with decomposition, and exhibit strong pleochroism. After remainining for a few hours, the compound gives up bromine, and it is also decomposed by dissolving in alcohol, glacial acetic acid, or ethyl acetate. It is insoluble in water, ether, chloroform, and light petroleum.

Anhydroecgonine dibromide hydrobromide,

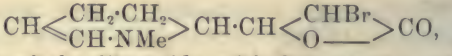
$$C_5NH_7Me\cdot CHBr\cdot CHBr\cdot COOH,HBr,$$

is obtained by the decomposition of the previous compound in a current of steam; it is deposited from alcohol, glacial acetic acid, or water in long, monoclinic prisms melting at 187—188° with decomposition. From dilute aqueous solution, tetragonal double pyramids are deposited, which contain 3 mols. H_2O and melt at 181—182° with decomposition. On exposure to air, these crystals become converted into the anhydrous modification.

Anhydroecgonine dibromide hydrochloride,

$$C_5NH_7Me\cdot CHBr\cdot CHBr\cdot COOH,HCl,$$

is formed by the action of silver chloride on the hydrobromide. It crystallises in long, monoclinic prisms melting at 173—174° with decomposition, and also in tetragonal octahedra, which contain water of crystallisation and melt at 169—170°. By the action of alkalis or alkaline carbonates on the salts of anhydroecgonine dibromide, methylamine, carbonic anhydride, and hydrogen bromide are eliminated, and dihydrobenzaldehyde is obtained. If, however, the action is allowed to proceed in the cold, several intermediate products may be isolated.

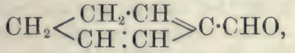
α-Bromecgonine lactone,  $\mathrm{CH}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH\cdot NMe}\end{matrix}>\mathrm{CH\cdot CH}<\begin{matrix}\mathrm{CHBr}\\ \mathrm{O}\text{———}\end{matrix}>\mathrm{CO}$, is prepared by treating a salt of the dibromide with 2 parts of a saturated solution of potassium carbonate, or by the action of ammonium hydroxide or sodium hydroxide at 0°. It is extremely soluble in water, insoluble in absolute alcohol, and crystallises from acetone in small, cubical crystals which melt at about 150° with evolution of carbonic anhydride. The *hydrochloride* is deposited from dilute aqueous solution in tetragonal octahedra which contain 3 mols. H_2O, and melt at 197—198° with decomposition; the compound crystallises from alcohol, from glacial acetic acid, or from concentrated aqueous solution in anhydrous, monoclinic prisms which melt at 203—204° with decomposition. The *hydrobromide* is also dimorphous; the anhydrous, monoclinic modification melts at 179°, and the tetragonal form melts at 174°. The *aurochloride*, $C_9H_{12}NO_2Br,HAuCl_4 + 1\frac{1}{2}H_2O$, crystallises from water in tufts of long, golden-yellow needles which melt at 211°; on exposure to air, the crystals become anhydrous and melt at 216°. The lactone does not yield a methyl salt; on boiling with water, carbonic anhydride is eliminated, and a compound of the formula $C_5NH_7Me\cdot C_3H_3O_3,HBr$ is formed in very small quantity; it crystallises from dilute alcohol in monoclinic prisms melting at 175°.

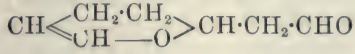
ω-Bromo-1-3-4-*methyltetrahydropyridylethylene*,

$$C_5NH_7Me\cdot CH\colon CHBr,$$

is prepared by heating a glacial acetic acid solution of the lactone in a sealed tube for 5 to 6 hours at 170°; the product is poured into water, and the solution neutralised with sodium carbonate and extracted with ether; on treating the ethereal solution with hydrochloric acid and auric chloride, the *aurochloride* is formed; it crystallises in short, yellow needles which melt at 174°. On boiling with water, the auric salt of methyltetrahydropyridylacetylene is formed (see below). The same base is also obtained by the fusion of the lactone, or by boiling it for some time with glacial acetic acid or acetic anhydride.

On boiling dibromecgonine dibromide hydrobromide with aqueous potassium carbonate, and distilling the solution in a current of steam, a yellow, oily liquid is obtained; this is dissolved in ether and the solution washed with hydrochloric acid; the acid liquid is neutralised with soda and extracted with ether; on evaporation, *methyltetrahydropyridylacetylene*, $C_5NH_7Me\cdot C{\vdots}CH$ remains as a colourless, basic, viscid liquid. The *aurochloride* crystallises from dilute alcohol in brownish-yellow cubes or flat, yellow needles which melt at 177·5—178·5°.

Dihydrobenzaldehyde,  $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH}\\ \mathrm{CH:CH}\end{matrix}>\mathrm{C\cdot CHO}$, is formed, together with the previous compound, from which it is separated in the manner described. It is best prepared by heating an aqueous solution of anhydroecgonine dibromide hydrobromide with 0·5 part of sodium carbonate at 60°; the product is distilled in a current of steam and the distillate extracted with ether. After washing with a few drops of hydrochloric acid, the ether is distilled, and the residue fractionated in a vacuum; the yield is 20 per cent. of the dibromide employed. Methylamine and anhydroecgonine hydrobromide are also formed. The aldehyde is obtained as a colourless oil which darkens on exposure to light, and has an intensely nauseous odour; it boils at 121—122° under a pressure of 120 mm., and is partly decomposed on distillation at ordinary pressures; sp. gr. = 1·0202 at 14·5°, and 1·0327 at 0°. It forms a crystalline compound with ammonia, reduces ammoniacal silver solution and potassium permanganate solution in the cold, and also reduces Fehling's solution on warming; it is not oxidised on exposure to air or oxygen, but becomes slowly converted into a resinous mass; concentrated sulphuric acid decomposes it in the cold. The formation of the aldehyde is explained by assuming that hydroxyl is substituted for the bromine in ω-bromomethyltetrahydropyridylethylene; the unstable group CH:CH·OH then changes into the more stable complex $CH_2\cdot CHO$, and, by the elimination of methylamine, the hypothetical compound



$$\mathrm{CH}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH}\text{——}\mathrm{O}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CHO}$$

is formed; this gives up the elements of water and yields dihydrobenzaldehyde. The aldehyde forms a crystalline compound on treatment with hydrogen sodium sulphite in the cold, which is readily soluble in water, but insoluble in alcohol or ether; on boiling with an alkaline carbonate, it is converted into benzaldehyde. *Dihydrobenzylidene phenylhydrazone* is prepared by the action of phenylhydrazine on dihydrobenzaldehyde, and is deposited from alcohol in small, yellow plates melting at 127—128°; the crystals exhibit strong pleochroism. *Dihydrobenzoxime* is obtained by the action of hydroxylamine on the aldehyde. The oily liquid which is formed consists of two isomeric compounds, which may be separated by treatment with light petroleum (b. p. 40—50°); the soluble compound, which is termed the β-oxime, crystallises on cooling, and melts constantly at 43—44°; the α-hydroxime is insoluble in light petroleum, and does not crystallise.

Dihydrobenzoic acid,

$CH_2<\begin{matrix}CH_2\cdot CH\\ CH:CH\end{matrix}>C\cdot COOH$, is prepared by the oxidation of the aldehyde with an ammoniacal solution of silver oxide; it is volatile with steam. On cooling an aqueous solution, it is deposited in feathery crystals which melt at 94—95°, and are more sparingly soluble in water than benzoic acid. The compound has an agreeable odour, and reduces ammoniacal silver solution, but does not react with Fehling's solution: it is converted into benzoic acid on strongly heating. The *silver salt* readily decomposes on exposure to light; like the *lead salt*, it is sparingly soluble in water. The salts of *barium*, *ammonium*, and the *alkali metals* readily dissolve in water, and crystallise from dilute alcohol, on the addition of ether, in silky, lustrous needles. The *copper salt* is soluble in ammonia with a green colour, and is deposited in green, nodular crystals. On treating dihydrobenzaldehyde with almost any other oxidising agent, it either remains unaltered, or is completely decomposed; with potassium permanganate, it yields benzoic acid. J. B. T.

The Stereochemical Isomerides of Paratolyl Phenyl Ketone. By A. HANTZSCH (*Ber.*, **23**, 2776—2780).—The further investigation of the oximes of paratolyl phenyl ketone (Abstr., 1890, 1273) has shown that the α-oxime may be converted into the β-compound simply by heating its alcoholic solution. The transformation is, however, very incomplete, and a large amount of the ketone is re-formed. Better results are obtained when the oxime is mixed with an equal weight of hydroxylamine hydrochloride, but even under these conditions a mixture of the two oximes is always obtained. As previously mentioned, the β-oxime is only slowly and incompletely converted into the benzyl ether on treatment with benzyl chloride; if, however, the bromide is employed, the reaction proceeds much more readily, and a purer product is obtained, which, after recrystallisation from amyl alcohol, melts at 51°. It also crystallises from ether in slender, silky needles, and if pure is not acted on by hot water or alcohol, or when hydrogen chloride is passed into its ethereal solution.

The acetyl derivative of the α-oxime has already been described by Auwers (Abstr., 1890, 503). If the β-oxime is dissolved in acetic anhydride at the ordinary temperature, and the solution allowed to evaporate spontaneously, *β-acetylparatolyl phenyl ketoxime*, $CPh(N\cdot OAc)\cdot C_7H_7$, crystallises out. The crystals resemble those of the α-compound, but are somewhat more acute. It cannot be obtained quite pure, as it readily passes into the α-acetyl derivative in the course of the usual processes of purification, especially in alcoholic solution; if the latter be warmed, the transformation is almost instantaneous and complete. This fact explains why Auwers (*loc. cit.*) was unable to obtain the β-oxime, for he adopted this method of purification, and therefore only obtained the α-compound. Phenyl isocyanate acts on both oximes, but with formation of one and the same additive compound, corresponding with the α-oxime and melting at 180°. The isomeric acetyl derivatives and phenyl isocyanate additive compounds of parabromobenzophenone are much more stable than the above; this, according to the author, is probably due to the influence of the methyl group. H. G. C.

Constitution of Cumenylpropionic Acid. By O. WIDMAN (*Ber.*, **23**, 3076–3080; compare Abstr., 1889).—*Orthobromocumenylacrylic acid*, $CHMe_2\cdot C_6H_3Br\cdot CH:CH\cdot COOH$ [$CH:CHMe:Br = 1:2:4$], is prepared from the corresponding amido-acid, but could not be obtained in a pure condition; it crystallises from dilute acetic acid in long, colourless needles melting at 134°. On reduction with hydriodic acid and phosphorus, it yields *orthobromocumenylpropionic acid*, $CHMe_2\cdot C_6H_3Br\cdot CH_2\cdot CH_2\cdot COOH$, crystallising from light petroleum in long, slender needles which melt at 55·5°, and yield cumenyl propionic acid by the action of sodium amalgam.

Orthochlorocumenylacrylic acid, $CHMe_2\cdot C_6H_3Cl\cdot CH:CH\cdot COOH$, crystallises from acetic acid in lustrous plates melting at 133—134°.

By the action of sodium nitrite and hydrobromic acid on amidopropylcinnamic acid, a compound is obtained which melts at 128°, and on reduction with phosphorus and hydriodic acid, yields the above described orthobromocumenylpropionic acid (m. p. 55·5°). An investigation of the orthamidopropylcinnamic acid showed it to be a mixture of two-thirds orthamidocumenylacrylic acid (m. p. 161°) and one-third metamidocumenylacrylic acid. It follows, therefore, that the so-called orthonitropropylcinnamic acid is also a mixture of ortho- and meta-nitrocumenylacrylic acids. Cumenylpropionic acid (m. p. 75·59°) is thus finally proved to be an isopropyl derivative.

J. B. T.

Perkin's Reaction. By O. REBUFFAT (*Gazzetta*, **20**, 158—162).—The condensation of aldehydes with organic sodium salts is generally supposed to take place without the acetic anhydride used taking any part in the reaction. The author finds that in his synthesis of phenylcinnamenylacrylic acid (Abstr., 1885, 1137) from cinnamaldehyde, sodium phenylacetate and acetic anhydride, if the reaction is interrupted as soon as the solution has been raised to the boiling point, and the product is thrown into cold water, an insoluble oil remains, which has the composition of *cinnamylidene diacetate*, $CHPh:CH\cdot CH(OAc)_2$, whilst the aqueous solution contains the whole of the phenylacetic acid used. The acetate crystallises from alcohol in large, colourless, nacreous plates, and melts at 84—85°. It is decomposed into cinnamaldehyde and acetic acid by distillation in steam, or by boiling with alkaline carbonates. It takes up 2 atoms of bromine forming an unstable compound, which, on steam distillation, yields Zincke's phenyl-β-bromacraldehyde (Abstr., 1884, 1343). If left for a long time, it is converted into a yellow syrup, which smells of cinnamaldehyde and acetic acid. The foregoing experiment renders it probable that the first step in Perkin's reaction is the formation of an acetate of the aldehydic radicle. S. B. A. A.

Methylresorcinolphthaloylic Acid. By E. QUENDA (*Gazzetta*, **20**, 127—132).—*Methylresorcinolphthaloylic acid*,

$$COOH\cdot C_6H_4\cdot CO\cdot C_6H_3(OH)\cdot OMe,$$

is obtained like the corresponding anisoïl and phenetoïl derivatives (see Grande, Abstr., 1890, 1128). A mixture of phthalic anhydride (12 grams), dimethylresorcinol (24 grams), and aluminium chloride (16 grams) is heated for about three hours on the water-bath, the product thrown into excess of cold water, and the precipitated acid extracted with ammonium carbonate, and reprecipitated with hydrochloric acid. It is then purified by repeated crystallisation from toluene and from water. The pure acid crystallises in light, colourless scales, dissolves sparingly in boiling water, but readily in hot toluene and in ether. It melts at 164—165°, forming a clear, yellowish-red liquid, and at a higher temperature dense, white, irritating fumes are evolved. A neutral solution of the ammonium salt gives precipitates with soluble salts of copper, zinc, mercury, lead, &c. The *silver* salt, $C_{15}H_{11}O_5Ag$, is obtained as a heavy, white precipitate, which is soon blackened and decomposed by light. The *barium* salt crystallises in anhydrous, yellowish nodules. S. B. A. A.

Gallic Acid, Tannin, and Oak Tannic Acids. By C. BÖTTINGER (*Annalen*, **259**, 132—136).—The author's attempts to prepare cyanhydrins and oximes from gallic acid and various tannins were unsuccessful, and no definite results were obtained. F. S. K.

Action of Phenylhydrazine on Tannin Extracts. By C. BÖTTINGER (*Annalen*, **259**, 125—132).—The true tannins combine with phenylhydrazine, yielding amorphous compounds, which have not been prepared in a pure condition, and which consequently have not been analysed; in their behaviour with acids, they show a certain resemblance to the osazones of the sugars.

On boiling an aqueous solution of a tannin extract with phenylhydrazine, carbonic anhydride is evolved, probably also nitrogen, and the phenylhydrazine is partially decomposed into ammonia and azobenzene, so that ammonia derivatives, as well as phenylhydrazine derivatives of the tannins, are formed. The following extracts were examined:—Sumach, vallonia, algarobilla, divi-divi, oak-wood, oak-bark, and pine-bark. F. S. K.

Manufacture of Decolorised Tannins: Zinc Tannate. By A. VILLON (*Bull. Soc. Chim.* [3], **3**, 784—786).—The liquor obtained by exhausting the crude material in the ordinary way is cooled at 2° for half an hour, and after filtering off extractives and tannins insoluble in the cold, 0·5 per cent. of zinc sulphate is added. The tannin of the liquor is now titrated, and for each kilo. present in the solution, 2·5 kilos. of zinc sulphate, dissolved in 12·5 litres of water, is added, and the whole is placed in a closed vat, furnished with a mechanical stirrer and steam coil, into which is passed the ammonia resulting from the decomposition of 2·5 kilos. of ammonium sulphate per kilo. of tannin present. After separation by a filter press of the precipitated zinc tannate, it is decomposed by dilute sulphuric acid, and to the liquor barium sulphide is added, until the zinc sulphate is completely precipitated as zinc sulphide and barium sulphate. On filtration, a liquor containing 20—30 per cent. of tannin, and almost free from colour, is obtained. The process is economical, since all the bye-products are capable of easy regeneration. T. G. N.

Diphenylsuccinic Acids. By R. Anschütz and P. Bendix (*Annalen*, **259**, 61—100).—Diphenylmaleïc anhydride, prepared from benzyl cyanide by Reimer's method (Abstr., 1882, 169), separates from ether in well-defined rhombic crystals, $a : b : c = 0{\cdot}69287 : 1 : 1{\cdot}35838$, boils at 236° (15 mm.), and is readily soluble in chloroform and benzene, but only sparingly in alcohol and ether. Attempts to convert this anhydride into diphenylfumaric acid were unsuccessful; when it is treated with hydrogen chloride in methyl or ethyl alcoholic solution, it is partially converted into an alkyl salt identical with that obtained from the silver salt of diphenylmaleïc acid, but a considerable quantity of the anhydride remains unchanged.

Diphenylmaleänil, $C_{22}H_{15}NO_2$, is easily obtained by heating the preceding compound with aniline at 120°; it crystallises from alcoholic chloroform in slender needles, melts at 174—175°, and boils at 293° (14 mm.). On hydrolysis with boiling potash, it is decomposed into diphenylmaleïc acid and aniline; the same change is brought about by boiling hydrochloric acid, but only very slowly. These experiments show that diphenylmaleïc anhydride is not converted into diphenylfumaric acid under conditions which lead to the transformation of maleïc into fumaric acid; it is doubtful whether the compound described by Rügheimer (Abstr., 1882, 1298) as diphenylfumaric acid is in reality this substance.

Both α- and β-diphenylsuccinic acids are formed when diphenylmaleïc anhydride is reduced with sodium amalgam in alkaline solution, as described by Reimer (*loc. cit.*), or with zinc and hydrochloric acid in alcoholic solution; the relative yield of the β-acid is greater when the reduction is carried out with zinc and hydrochloric acid. The two acids are most conveniently separated by means of their barium salts.

Barium α-diphenylsuccinate, $C_{16}H_{12}O_4Ba + 2H_2O$, is obtained by precipitating a solution of the ammonium salt with barium chloride; it is soluble in 312 parts of water at 17—18°. A sparingly soluble salt containing 4 mols. of water is formed when barium hydroxide is added to a dilute solution of the ammonium salt.

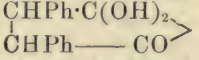
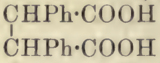
Barium β-diphenylsuccinate, $C_{16}H_{12}O_4Ba + 7H_2O$, separates in well-defined crystals when a solution of the barium salt of the β-acid is evaporated at 100°; it is soluble in 4·742 parts of water at the ordinary temperature.

Both α- and β-diphenylsuccinic acid form colourless silver salts, which, when dried at 100°, have the composition $C_{16}H_{12}O_4Ag_2$; when these silver salts are treated with ethyl iodide at 100°, they are converted into ethyl salts, identical with the compounds obtained by Reimer (*loc. cit.*), by treating the corresponding acids with alcohol and sulphuric acid. The ethyl salt of the α-acid melts at 84°, that of the β-acid at 140—141°.

α-Diphenylsuccinic acid dissolves in cold acetic chloride with evolution of hydrogen chloride, and, after evaporating the solution at 100°, there remains an oily mixture of the anhydrides of the α- and β-acids, which gradually becomes crystalline; this product separates from ether in well-defined crystals, melts at 115—116°, and boils at 240° (about 15 mm.), the distillate gradually solidifying. When boiled with water, it yields about 96·5 per cent. of the α-acid, and 3·5 per cent. of the β-acid, even when in its preparation from the acid the temperature is kept below 36° throughout the various operations; when treated with potash, it gives 85·8 per cent. of the α-acid, and 14·8 per cent. of the β-acid. The same mixture of anhydrides is obtained from the barium salt of the α-acid in like manner.

β-Diphenylsuccinic acid is not acted on by acetic chloride in the cold, but at 100° it yields a mixture of anhydrides which has the same melting point and other physical properties as that obtained from the α-acid, but which, on boiling with water, gives 74·81 per cent. of the α-acid, and 18·5 to 26·1 per cent. of the β-acid. When silver or barium β-diphenylsuccinate is treated with acetic chloride, a mixture of the anhydrides is formed which melts at 110—111°, and on boiling with water, gives 65—70 per cent. of the β-acid, and 25—40 per cent. of the α-acid.

The mixture of anhydrides obtained by distilling α- or β-diphenylsuccinic acid under reduced pressure (14 mm.) melts at 112—113° and in its behaviour with solvents, &c., it resembles that produced by treating the acids with acetic chloride; when boiled with water, it yields about 90 per cent. of the α-acid, and 10 per cent. of the β-compound.

When the α-acid is heated at temperatures ranging from 150 to 185°, about 50 per cent. is converted into anhydride, and about 50 per cent. into the β-acid; the β-acid, on the other hand, does not lose water below 185°. These experiments prove the existence of two isomeric diphenylsuccinic anhydrides, but owing to the great similarity in properties, the two compounds cannot be separated; the existence of two anhydrides proves, however, that the isomerism of the two acids cannot be explained by assuming, as Roser has done, that they have the constitution 
$\begin{array}{l} \mathrm{CHPh{\cdot}C(OH)_2} \\ | \\ \mathrm{CHPh{-\!\!-}CO} \end{array}\!\!>$
and 
$\begin{array}{l} \mathrm{CHPh{\cdot}COOH} \\ | \\ \mathrm{CHPh{\cdot}COOH} \end{array}$
respectively, and it seems more probable that the relationship between them is the same as that which exists between the two hydrobenzoïns.

Diphenylsuccinanil, $C_{22}H_{17}NO_2$, is obtained when the anhydride, prepared either from α- or β-diphenylsuccinic acid by means of acetic chloride, is heated with aniline; it can also be obtained by reducing diphenylmaleänil. It crystallises from hot benzene in colourless needles melting at 226—227°, and from glacial acetic acid in larger needles melting at 230—231°.

Diphenylsuccinanilic acid, $C_{22}H_{19}NO_3$, is produced when the preceding compound is boiled with barium hydroxide; it crystallises from dilute alcohol in colourless needles, and melts at 220°. It is not changed by warm concentrated alcoholic potash, but it is reconverted into the anil by glacial acetic acid, hydrogen chloride, and alcoholic sulphuric acid.

F. S. K.

Crystallographic Proof of the Identity of Pyranilpyroïnlactone and Citraconanil. By R. Anschütz (*Ber.*, **23**, 2979—2981; see also Abstr., 1890, 1102).—By the slow evaporation of the ethereal solution of citraconanil obtained in different ways, the author has succeeded in obtaining it in well developed crystals. Hintze and Jennsen have examined crystallographically preparations obtained (1) from β-anilidopyrotartaric acid (Reissert's pyranilpyroïnlactone), (2) from aniline and citraconic acid, (3) from pseudoitaconanilic acid. The measurements show conclusively that the substances obtained by all three methods are identical, the crystals belonging to the monosymmetric system ($a : b : c = 2{\cdot}7575 : 1 : 1{\cdot}8152$, $\beta = 51° 17'$). The optical properties of all three were also found to be almost identical, three corresponding plates giving the following numbers :—

	No. 1.	No. 2.	No. 3.
2Ha........	11° 6′	11° 22′	11° 35′

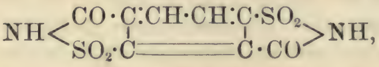
H. G. C.

Paranitro-orthotoluenesulphonic Acid. By J. Hausser (*Bull. Soc. Chim.* [3], **3**, 797—799).—Paranitrotoluene (200 grams) is slowly added to sulphuric acid containing 44 per cent. sulphuric anhydride (260 grams), the energetic reaction being modified by cooling with ice, and then completed by heating the mixture at 150°. The product is added to water (1500 grams), and after removing the excess of sulphuric acid by calcium carbonate, the solution is concentrated until the sulphonic acid crystallises out, the yield being 64 per cent. The author confirms Jennsen's researches (this Journal, 1874, 479), and finds that the acid decomposes the sulphates of zinc and copper forming nitrosulphonates and liberating sulphuric acid. Nitrotoluenemetasulphonic acid, which may be prepared in a similar manner, is an analogous substance. T. G. N.

Iodometaxylenesulphonic Acid. By C. Bauch (*Ber.*, **23**, 3117—3119).—The iodometaxylenesulphonic acid prepared by Hammerlich (Abstr., 1890, 1106) has the formula [$Me_2 : I : SO_3{\cdot}H = 1 : 3 : 4 : 6$], since, on fusion with potash, it yields a dihydroxy-derivative which melts at 146° and is identical with the compound obtained by Wischin (compare following abstract). The sulphonamide, prepared after elimination of the iodine, melts at 137°, and therefore has the formula [$Me_2 : SO_2NH_2 = 1 : 3 : 4$]. J. B. T.

Metaxylenedisulphonic Acid. By R. Wischin (*Ber.*, **23**, 3113—3117).—*Metaxylenedisulphonic acid*, [$Me_2 : (HSO_3)_2 = 1 : 3 : 2 : 4$], is prepared by heating metaxylene with 4 parts of fuming sulphuric acid at 150°; on pouring into water, small crystals separate which cannot be purified by crystallisation from dilute sulphuric acid. The *disulphochloride* crystallises from ether in needles melting at 129°. The constitution of the compound is proved by the production of dichlorometaxylene (b. p. 228°), on heating with phosphorus pentachloride at 180°. The *sodium salt* is readily soluble in water. On oxidation with potassium permanganate, it yields a *disulphisophthalic acid*, which is deposited from alcohol in small, granular crystals melting at 250°. The *barium sulphonate* crystallises from water in plates. The *sulphonamide* is deposited from water in silky, lustrous needles which melt at 249°.

Dihydroxyxylene [$Me_2 : (OH)_2 = 1 : 3 : 2 : 4$] is obtained by fusing the sulphochloride with potassium hydroxide, and may be purified by sublimation; it is deposited in slender, white needles melting at 146°, and is very readily soluble in water, alcohol, or ether; an intense violet colour is produced with ferric chloride; on heating with phthalic anhydride and dissolving the product in soda, a green fluorescence is observed. *Disulphamine-isophthalic anhydride*,



$$NH<\begin{array}{l}CO\cdot C{:}CH\cdot CH{:}C\cdot SO_2\\ SO_2\cdot C{=\!=\!=\!=\!=}C\cdot CO\end{array}>NH,$$

is prepared by heating the disulphonamide with potassium permanganate solution, and decomposing the resulting potassium salt with sulphuric acid; the anhydride crystallises from alcohol, melts at 225°, is very sparingly soluble in water, and exceedingly bitter to the taste.

Metaxylenedisulphonethylamide, from the disulphochloride and ethylamine, crystallises from water in silky, lustrous needles which melt at 135°.

Bromoxylenedisulphonic acid [$Me_2 : Br : (HSO_3)_2 = 1 : 3 : 4 : 2 : 6$] is prepared by the action of fuming sulphuric acid on bromo-xylene [$Me_2 : Br = 1 : 3 : 4$]; both the acid and its salts crystallise with great difficulty. The *sulphochloride* is obtained from ether in long, white crystals melting at 160°. The *sulphonamide* is deposited from water in needles melting at 265°.

Bromodihydroxyxylene, obtained by the fusion of the acid with potassium hydroxide, forms white crystals, melts at 126°, and gives a violet colour with ferric chloride.

Chloro-xylenedisulphonic acid resembles the bromo-derivative in properties and constitution. The *sulphochloride* crystallises from ether in white needles melting at 155°. The *sulphonamide* is deposited from water in silky, lustrous needles which melt at 270°.

Chlorodihydroxyxylene is obtained by sublimation in white needles which melt at 106°, and give a violet colour with ferric chloride.

J. B. T.

Action of Thionyl Chloride on Secondary Aromatic Amines. By A. Michaelis and E. Godchaux (*Ber.*, **23**, 3019—3023; compare Abstr., 1890, 610).—*Thionylmethylaniline*, $SO(C_6H_4\cdot NHMe)_2$, is prepared by adding an ethereal solution of thionyl chloride to a mixture of aluminium chloride and methylaniline, dissolved in the same medium; the solution is well cooled and poured into cold water, the ether separated, and the aqueous solution filtered and treated with excess of soda; the precipitate thus obtained is boiled with alcohol, and the alcohol evaporated; the residue is dissolved in chloroform, and, on adding light petroleum, it crystallises out in stellate groups of colourless needles which melt at 154° and readily assume a blue tint. *Nitrosothionylmethylaniline*, $SO(C_6H_9\cdot NOMe\cdot NO)_2$, is obtained by the action of sodium nitrite and hydrochloric acid on the preceding compound, and is deposited from alcohol in colourless needles melting at 171°.

Thiomethylaniline, $S(C_6H_4NHMe)_2$, is formed by the reduction of the thionyl derivative with sodium in alcoholic solution; it crystallises from a mixture of ether and light petroleum in long, yellow, transparent needles which melt at 60°, and are readily soluble in chloroform, ether, or alcohol. *Nitrosothiomethylaniline*, $S(C_6H_4{\cdot}NMe{\cdot}NO)_2$, from sodium nitrite and thiomethylaniline, crystallises in yellow, lustrous plates which melt at 133°, and are very sparingly soluble in cold alcohol. J. B. T.

New Synthesis of Indigo. By L. LEDERER (*J. pr. Chem.* [2], **42**, 383).—2 grams of phenylglycocine are stirred into 8—10 grams of fused sodium hydroxide, and the fusion maintained until the colour becomes pure orange, when the reaction is over. The melt is dissolved in much water, when pure indigo-blue is separated. A. G. B.

Synthesis of Indigo and Allied Dyes. By K. HEUMANN (*Ber.*, **23**, 3043—3045).—Phenylglycocine is heated in absence of air with 2 parts of potassium hydroxide at 260°; the fused mass becomes brownish-orange; it is allowed to cool, dissolved in water, and a stream of air drawn through the solution; an immediate precipitation of indigo occurs. Care must be taken not to continue the fusion too long, or decomposition takes place; small portions are therefore withdrawn from time to time and dissolved in water, the heating being immediately stopped as soon as the formation of indigo is observed. Sodium hydroxide may be substituted for potassium hydroxide, but the reaction takes place at a much higher temperature. Experiments with other dehydrating agents were unsuccessful. The reaction may be explained by assuming that, by the elimination of water from phenylglycocine, pseudindioxyl, $C_6H_4{<}{\substack{CO\\NH}}{>}CH_2$, is formed, and that this yields indigo on oxidation. J. B. T.

Desmotropy in Phenols. By J. HERZIG and S. ZEISEL (*Monatsh.*, **11**, 413—420; compare Abstr., 1888, 822; 1889, 247 and 966).—On heating diresorcinol (1 mol.) in alcoholic solution with potash (8 mols.) and ethyl iodide (8 mols.) in a reflux apparatus for several hours, the authors obtained, as the chief product, a viscid, brownish oil, insoluble in potash. When shaken with cold alcohol, a portion of this substance dissolves, and may be obtained on evaporation of the solvent. After several recrystallisations from hot alcohol, it is obtained in scales melting constantly at 90—92°, and is shown by analysis to be *ethyldiresorcinyl tetrethyl ether*, $C_{12}H_5Et(OEt)_4$. On heating this compound with hydriodic acid, *ethyldiresorcinol*, $C_{12}H_5Et(OH)_4$, is formed, but, owing to its instability, it cannot be obtained in a pure state. *Tetracetylethyldiresorcinol*, $C_{12}H_5EtAc_4$, is readily prepared by heating the product of the action of hydriodic acid on ethyldiresorcinyl tetrethyl ether with acetic anhydride. It crystallises from alcohol in needles which melt at 135—138°.

That portion of the oil which is insoluble in alcohol consists of *diresorcinyl tetrethyl ether*, $C_{12}H_6(OEt)_4$, and crystallises from hot alcohol in scales which melt at 112—114° (compare Pukall, Abstr., 1887, 660—661).

These results show that in diresorcinol two hydroxyl groups of a benzene nucleus occupy, relatively to each other, the meta-position, and that ethylation is induced by the mobility of their hydrogen atoms, in the same way as the authors have previously shown (*loc. cit.*) obtains in the case of other metaphenols. G. T. M.

Diphenyldiethylene Derivatives. By O. REBUFFAT (*Gazzetta*, **20**, 154—157).—*Diphenyldiethylene*, $CHPh{:}CH{\cdot}CH{:}CHPh$, synthetically prepared by the author (Abstr., 1885, 1137), crystallises from alcohol in large, colourless, micaceous plates, melts at 147—148°, and distils unaltered at 250°. It is sparingly soluble in ether, but readily in alcohol and carbon bisulphide.

Tetrabromodiphenyldiethylene, prepared by treating an ethereal solution of the hydrocarbon with excess of an ethereal solution of bromine, crystallises in white scales which are unaffected by prolonged exposure to air and light; it blackens and melts at 230°.

The *dibromo*-derivative, $CHPhBr{\cdot}CHBr{\cdot}CH{:}CHPh$, is prepared by mixing the theoretical quantities of its constituents in ethereal solution in the cold, and allowing the mixture to remain. It forms tufts of colourless, acicular crystals, and melts at 147—148°, decomposing if not quite pure. It combines with some difficulty with two atoms of bromine forming the tetrabrominated derivative.

When a solution of diphenyldiethylene in carbon bisulphide is treated with a solution of bromine in the same solvent in the proportion required for the formation of a tetrabromide, the liquid is decolorised after some time, a small quantity of the hydrocarbon being deposited; on distillation, the dibromo-derivative passes over together with a brominated compound, intermediate in composition between the di- and tetra-bromo-derivatives. This substance crystallises from carbon bisulphide in long prisms, and melts at 198°, previously softening at 190°. S. B. A. A.

Synthesis of Benzylcinnamic Acid. By A. OGLIALORO (*Gazzetta*, **20**, 162—164).—*Benzylcinnamic Acid*, $C_{12}H_{14}O_2$.—A mixture of sodium hydrocinnamate and benzaldehyde in molecular proportion is heated with an excess of acetic anhydride for six hours at 160°, and the unaltered anhydride and the phenylpropionic acid are then removed by treating the product with ether and hot water respectively. The residue, after being purified by extraction with boiling light petroleum, crystallises from absolute alcohol in large, white needles which melt at 158°. The most probable constitution for this compound is that of a benzylcinnamic acid, $CHPh{:}C(CH_2Ph){\cdot}COOH$.

S. B. A. A.

Naphthyl Sulphides. By F. KRAFFT and E. BOURGEOIS (*Ber.*, **23**, 3045—3049; compare Abstr., 1890, 1311).—$\alpha\alpha$-Dinaphthyl sulphide may be prepared from bromonaphthalene and the lead salt of α-naphthyl mercaptan in the manner previously described. *Phenyl-*

α-naphthyl sulphide, $C_{10}H_7{\cdot}SPh$, is obtained in the same way by heating α-bromonaphthalene with the lead salt of phenyl mercaptan, at 240° for 2—3 hours; it crystallises from alcohol in hard, colourless, lustrous prisms which melt at 41·5°, and boil at 218° under a pressure of 14 mm. The yield is over 50 per cent. of the lead salt employed; on oxidation, the corresponding sulphone is obtained.

Phenyl-β-naphthyl sulphide, $C_{10}H_7{\cdot}SPh$, is formed, together with diphenyl sulphide and ββ-dinaphthyl sulphide, from monobromobenzene and the lead salt of β-naphthyl mercaptan; it crystallises from alcohol in stellate groups of small, white needles, or in lustrous plates, which melt at 51·5°, and boil at 224° under a pressure of 14 mm. The yield is 25 per cent. of theory, and the corresponding sulphone is obtained on oxidation. J. B. T.

Action of Aromatic Bases on Naphthol Violet. By R. HIRSCH and F. KALCKHOFF (*Ber.*, **23**, 2992—2994).—A new colouring matter related to naphthol violet has recently been described by Witt (Abstr., 1890, 1307), who regards it as being formed simply by the action of heat on the last-named colouring matter. The authors had also previously observed that, under certain circumstances, preparations of naphthol violet have an unusually blue shade. According to present ideas, the colouring matter has the constitution $C_{10}H_6{<}\genfrac{}{}{0pt}{}{N}{O}{>}C_6H_2{\cdot}NMe_2,HCl$, and is formed from nitrosodimethylaniline and β-naphthol according to the equation

$$C_{10}H_8O + C_8H_{11}N_2OCl = C_{18}H_{15}N_2OCl + H_2O + H_2.$$

The hydrogen thus set free reduces another portion of nitrosodimethylaniline to amidodimethylaniline, and the authors regarded it as probable that the blue colouring matter was formed by the further action of the latter on naphthol violet, and they, in fact, succeeded in thus obtaining a colouring matter identical in every respect with that described by Witt. In place of amidodimethylaniline, other aromatic bases, and even ammonia, may be employed, well-defined colouring matters being thus obtained. The compound from aniline crystallises in brown needles which melt at 256° and dissolve in concentrated sulphuric acid with a violet coloration. The base from paratoluidine resembles it very closely, but melts at 250°, whilst that from α-naphthylamine has a yellowish-brown colour in sulphuric acid solution. The yield does not, as a rule, amount to more than 50 per cent.

The constitution of these colouring matters has not yet been ascertained, but they are probably formed in a similar manner to the quinoneanilides. H. G. C.

Naphthoic Acids. By Å. G. EKSTRAND (*J. pr. Chem.* [2], **42**, 273—304; compare Abstr., 1889, 52, 152).—This paper is largely a reprint of what has already appeared. The nitro-β-naphthoic acids are best obtained as follows:—β-Naphthoic acid is gently warmed with nitric acid of sp. gr. 1·42 (two parts) until red fumes cease to appear, and the product is washed with water, dissolved in soda, and the sodium salt crystallised; the acids are then liberated from the recrystallised salts by hydrochloric acid, dissolved in alcohol, and converted into their ethyl salts by dry hydrogen chloride; the ethyl salts are separated by light petroleum, in which that of the acid of m. p. 288° is sparingly soluble, the residue from the mother liquor being recrystallised from benzene, and the mixed tables (ethyl salt of acid of m. p. 288°) and needles (ethyl salt of acid of m. p. 293°) separated by hand.

Nitro-β-naphthoic acid (m. p. 293°, Abstr., 1885, 905) dissolves in 660 parts of alcohol at the ordinary temperature. The barium salt crystallises with 4 mols. H_2O; the calcium salt (with $3\frac{1}{2}$ mols. H_2O) dissolves in 930 parts of water at the ordinary temperature. When the acid is oxidised by potassium permanganate, a non-nitrogenous acid is obtained which crystallises in slender needles and melts at 200°; it has not been identified, but its formation is a strong indication that the nitro- and carboxyl-groups are not in the same benzene nucleus. Nitro-β-naphthoic acid gives no dinitronaphthalene when treated with nitric acid, whereas nitro-α-naphthoic acid does. When amido-β-naphthoic acid (m. p. 232°, *loc. cit.*) is heated with barium oxide, α-naphthylamine is obtained; thus the constitution of the nitro- acid is $[NO_2 : COOH = 1' : 2$ or $4' : 2]$. *Acetamido-β-naphthoic acid* crystallises in small tables melting at 291°.

By the action of chlorine on amido-β-naphthoic acid (m. p. 232°) in hot glacial acetic acid in the presence of iodine, a substance insoluble in water and alcohol is obtained, which crystallises from glacial acetic acid in orange needles melting with intumescence at 235°; the analysis of this substance agrees fairly well with the formula $OH{\cdot}C_{10}H_3Cl_5{\cdot}COOH$; if the treatment with chlorine is continued, the product crystallises in pale-red needles which melt with intumescence at 238°. By chlorinating the amido-acid in the cold, and treating the product with sulphurous anhydride, a substance containing less chlorine is obtained; it crystallises in brownish tables which melt about 234°; when further chlorinated, it melts at 237°; its formula is uncertain, but a calcium salt (with 5 mols. H_2O) has been obtained in yellow needles. Two other chlorine derivatives, the one crystallising in orange-red tables and melting at 220°, and the other, a brick-red powder melting at 277°, have also been obtained.

Dinitro-β-naphthoic acid (m. p. 248°, Abstr., 1884, 1361) dissolves in 61 parts of alcohol at the ordinary temperature. The *ammonium* (with 1 mol. H_2O), *sodium* (with 4 mols. H_2O), *barium* (with 8 mols. H_2O), and *calcium* (with 5 mols. H_2O) salts are described. By treating this acid with a large excess of hydrogen sulphide in ammoniacal solution, a dark-brown, infusible powder is obtained; it cannot be freed from sulphur, but it appears to be a diimido-β-naphthoic acid, $COOH{\cdot}C_{10}H_5(NH)_2$ (compare Abstr., 1889, 153; 1886, 948; 1887, 373). From analogy with the dinitro-α-naphthoic acid (m. p. 265°), the author ascribes the constitution $[(NO_2)_2 : COOH = 1' : 1 : 2$ or $4' : 4 : 2]$ to this acid.

Diamido-β-naphthoic acid, obtained by reducing the above dinitro-acid with ferrous sulphate in ammonia, crystallises in greenish-yellow needles which melt at 202°, and partially sublime; the *calcium salt* and the *monohydrochloride*, melting above 285°, were obtained.

Nitro-β-naphthoic acid (m. p. 288, Abstr., 1885, 905) dissolves in 390 parts of alcohol at the ordinary temperature. The ethyl salt melts at 121°, not 122°. The *ammonium*, *barium* (with 8 mols. H_2O), and *calcium* (with 4½ mols. H_2O) salts are described. Oxidation with permanganate and treatment of the amido-acid with calcium oxide lead to the same conclusion as in the case of the β-nitro-acid (see above). *Calcium amido-β-naphthoate* crystallises with 4 mols. H_2O. *Acetamido-β-naphthoic acid* crystallises in slender needles which melt at 258°; the *diacetyl derivative* melts at 181°. *Nitracetamido-β-naphthoic acid* forms slender needles melting at 270°. When the amido acid is treated with chlorine in glacial acetic acid in presence of iodine, a product is obtained which crystallises in colourless needles and melts with intumescence at 258°; it would appear from its formula, $OH{\cdot}C_{10}H_4Cl_4{\cdot}COOH$, to be a dichloride of a dichloroxy-β-naphthoic acid. In another experiment, colourless tables of the formula $OH{\cdot}C_{10}H_3Cl_3{\cdot}COOH$, and melting at 237°, were obtained.

Dinitro-β-naphthoic acid (m. p. 226°, Abstr., 1884, 1361) dissolves in 57 parts of alcohol at the ordinary temperature; the *ammonium salt* (with 1 mol. H_2O) dissolves in 285 parts, and the *calcium salt* (with 4 mols. H_2O) in 1740 parts of water at the ordinary temperature; the *barium salt* (with 6 mols. H_2O) is described.

Nitramido-β-naphthoic acid is obtained by treating an ammoniacal solution of the dinitro-acid (m. p. 226°) with hydrogen sulphide, adding acetic acid, digesting the precipitate with hydrochloric acid, and decomposing the solution thus obtained by ammonia; it forms stellate needles and melts at 235°; its *hydrochloride* forms slender, red needles.

Diamido-β-naphthoic acid is obtained by reducing the dinitro-acid (m. p. 226°) with ferrous sulphate in ammonia; it melts about 230°, but with blackening, and forms small, six-sided crystals. The *calcium salt* (with 4½ mols. H_2O) and the *dihydrochloride* are described.

The ethyl salt of a third nitro-acid remains in the mother liquor of the benzene solution in the preparation of the above nitro-acid (see beginning of the abstract). The *nitro-β-naphthoic acid* corresponding with this ethyl salt crystallises in stellate needles which melt, although not sharply, at 285°; the *ethyl salt* melts at 75°.

A. G. B.

Dry Distillation of Terpenylic Acid. By C. Amthor and G. Müller (*J. pr. Chem.* [2], **42**, 385—399).—By the dry distillation of terpenylic acid, Amthor (Abstr., 1882, 44) obtained a syrupy acid, teracrylic acid, a lactone boiling at 202—204°, and a lactone, $C_7H_{12}O_2$, boiling at 210—212°; but Fittig and Kraft (Abstr., 1882, 42) obtained no lactone. The authors have, therefore, reinvestigated the subject.

100 parts of boiling ether dissolve 3·856 parts of terebic acid, and the same quantity of cold ether dissolves 1·698 parts; the following is therefore a better method for separating this acid from terpenylic acid than that previously adopted (*loc. cit.*):—The mixed acids are heated to 80—90°, at which temperature most of the terebic acid remains unmelted, and is separated from the molten terpenylic acid by filtration through cotton-wool in a hot water funnel; the terpenylic

acid is then crystallised from hot water, and again heated until most of it is melted, when warm water is added and the solution filtered through cotton-wool; some of the crystals which separate on cooling are then dried on a microscope slide, heated to 80—90°, and examined under the microscope for any still solid particles of terebic acid. The melting and solution in water are repeated until no more terebic acid is detected in the crystals examined in this way.

Barium diterpenylate crystallises with 2 mols. H_2O (Abstr., 1882, 43), one of which is lost over sulphuric acid, and both at a high temperature, although not without partial decomposition.

The investigation of the products of the distillation of terpenylic acid was carried out on much the same lines as previously (Abstr., 1882, 44); the acid was not perfectly dry when distilled, still containing its water of crystallisation (1 mol.). The products isolated were teracrylic acid (b. p. 218°), a syrupy acid, and a very small quantity of other acids; a very little heptalactone (?) (b. p. 210—213°); and various neutral oils, soluble and insoluble in water, among which was an oxetone, $C_{13}H_{24}O_2$.

Fittig and Kraft probably overlooked the lactone produced in the distillation, having used too little terpenylic acid.

Heptolactone boils at 218° (Fittig and Kraft, 220°; Amthor, 202—204°).
A. G. B.

Methyldipyridyls. By A. Heuser and C. Stoehr (*J. pr. Chem.* [2], **42**, 429—440).—Anderson (*Annalen*, **105**, 344) obtained a substance, which he called parapicoline, by the action of sodium on (impure) picoline. More recently Ahrens, (Abstr., 1889, 59) obtained a base which he called dipicolyl by the same process, but his picoline was not free from higher homologues. The authors have obtained a pure product and designate it as αα-dimethyldipyridyl.

αα-Dimethyldipyridyl, $C_{12}H_{12}N_2$, is prepared by adding thin strips of sodium (10 grams) to α-picoline (b. p. 128°, 20 grams) in a flask and gently warming the mixture, after 7—8 days, in a reflux apparatus. Water is then added to the reaction mass, an operation requiring great care as unaltered sodium is liable to remain enclosed in the mass and to cause an explosion, and the separated oil is distilled; ammonia and unaltered picoline come off below 150°, and then practically nothing distils until 300°. All that distils above 300° is redistilled, when the greater portion comes over at 303—306°; this portion is dissolved in absolute alcohol and converted into hydrochloride by a current of dry hydrogen chloride; the hydrochloride is recrystallised, decomposed by aqueous sodium carbonate, and the free base extracted with ether. This base crystallises from water in large, lustrous, white leaves, with 4 mols. H_2O, which are lost over sulphuric acid; the crystals melt at 37—38°, and the anhydrous substance at 84°. It dissolves in most solvents; like other pyridine bases, it is less soluble in hot than in cold water, and is separated from its aqueous solution by alkalis; it is specifically heavier than water, and has a characteristic odour. Its solutions give a yellow colour with potassium ferrocyanide, and brown-red tables gradually separate from the solution. The *hydrochloride* crystallises in colourless leaves, and dissolves easily in water and sparingly in alcohol; the *picrate* crystallises in sparingly soluble yellow tables, and melts with decomposition at 240°; the *stannochloride* forms prismatic, yellow needles which melt at 179—180°; the *zinc salt* and the *platinochloride* are described; the latter is sparingly soluble; the *aurochloride* forms needles, darkens at 200°, and melts at 209—210° (compare Ahrens, *loc. cit.*); the *mercurochloride* crystallises in serrated leaves which darken at 210° and melt at 220°.

α-Methyldipyridyl-α-carboxylic acid, $C_5NH_3Me{\cdot}C_5NH_3{\cdot}COOH$, obtained by oxidising αα-dimethyldipyridyl with potassium permanganate, crystallises in pale yellow needles (with 5 mols. H_2O); it is freely soluble in hot water and alcohol, and its solutions give a reddish-yellow colour with ferrous sulphate; the anhydrous acid melts at 193° giving off carbonic anhydride.

α-Methyldipyridyl, $C_5NH_3Me{\cdot}C_5NH_4$, is formed when the above mentioned carboxylic acid is heated with glacial acetic acid in a sealed tube at 180—190° for 2—3 hours; the acetic acid is evaporated, and the base liberated by sodium carbonate and extracted with ether. It is more soluble in water than dimethyldipyridyl, and melts at 94°; it will be treated of in a future communication. A. G. B.

α-Picoline and α-Isobutylenepyridine. By C. Stoehr (*J. pr. Chem.* [2], **42**, 420—428).—α-Picoline was obtained from animal oil by treating the hydrochloric acid solution of the fraction 128—133° with mercuric chloride and recrystallising the mercurochloride formed. It boils at 128°. The platinochloride never contains any water of crystallisation, whatever the circumstances under which it is crystallised (compare Weidel, Abstr., 1880, 269; Seyfferth, *J. pr. Chem.* [2], **34**, 248); it crystallises in monoclinic tables, $a : b : c = 0{\cdot}6636 : 1 : 0{\cdot}9078$; $\beta = 72° 46'$; it melts with decomposition at 195°, not 178° (Lange, Abstr., 1886, 256; and others), and is more soluble in water than β-picoline platinochloride. Impure α-picoline (b. p. 128—134°) gives a platinochloride which crystallises with 1 mol. H_2O, melts at 195°, and is nearly similar in crystalline form [$a : b : c = 0{\cdot}9758 : 1 : 1{\cdot}3270$; $\beta = 76° 47'$] to the platinochloride previously described as that of α-picoline (*loc. cit.*).

α-Isobutylenepyridine, $C_9H_{11}N$, is obtained by heating α-picoline (8 grams) with acetone (5 grams) and some zinc chloride in a sealed tube at 250—260° for 10 hours; the product is acidified with hydrochloric acid, extracted with ether, and, after heating to expel ether, distilled with steam; solid sodium hydroxide is then added and the liberated bases distilled, dried by potassium hydroxide, and redistilled. The greater part of the distillate, boiling below 140°, is unaltered α-picoline; the rest is twice fractionated, and the portion boiling between 190—210° converted into mercurochloride, from which the isobutylenepyridine is liberated by potassium hydroxide. It boils at 200°, is very sparingly soluble in water, has a blue fluorescence and peculiar odour; its aqueous solution becomes turbid from separation of the base at the temperature of the hand, and it is volatile with steam. Its sp. gr. at 0°/4° is 0·9715. The *hydrochloride* crystallises in prisms melting at 140—141°, and soluble in alcohol and water; the *platinochloride* forms needles or prisms (with 2 mols. H_2O), and melts, when anhydrous, at

163—164° with decomposition; the *aurochloride* is unstable, and melts at 135—137°; the *mercurochloride* is sparingly soluble, and crystallises in long, slender, lustrous needles which melt at 144—145°; the *picrate* forms small, yellow needles, melts at 177°, and is sparingly soluble. A. G. B.

Diethylmuscarinepyridine. By H. LOCHERT (*Bull. Soc. Chim.* [3], **3**, 858—861).—*Diethylmuscarinepyridine bromide*

$$C_5NH_5Br{\cdot}CH_2{\cdot}CH(OEt)_2,$$

is obtained by heating a mixture of bromacetal and pyridine, in molecular proportion, at 80° for 10 days; on cooling, the compound crystallises out in deliquescent, nacreous scales which are very soluble in water and in alcohol. With platinum tetrabromide, it forms a red, amorphous precipitate, which is almost insoluble in water, completely insoluble in alcohol.

On treating diethylmuscarinepyridine bromide in aqueous solution with moist silver oxide, a colourless, strongly alkaline liquid is obtained, which neither crystallises on concentration nor forms crystalline salts, concentration of the solutions yielding syrupy liquids. *Diethylmuscarinepyridine*, $OH{\cdot}C_5NH_5{\cdot}CH_2{\cdot}CH(OEt)_2$, as thus obtained, precipitates the hydroxides of silver and of copper from solutions of their salts.

Further communications on other muscarine derivatives are promised, as also on the synthesis of muscarine itself by means of bromacetal and trimethylamine. T. G. N.

Tribromoquinolines. By A. CLAUS and P. HEERMANN (*J. pr. Chem.* [2], **42,** 327—346).—The generic similarity between 3 : 4′-dibromoquinoline and the tribromoquinoline described by Claus and Welter (Abstr., 1890, 1320), and the fact that the latter can be obtained by brominating 4′-bromoquinoline, settles the orientation of two of the bromine atoms in this tribromoquinoline. The position of the third bromine atom is now settled, for the authors have succeeded in obtaining the same tribromoquinoline by heating 1 : 3-dibromoquinoline hydrobromide dibromide according to Claus' and Collischonn's method (Abstr., 1887, 158); this is therefore 1 : 3 : 4′-*tribromoquinoline.* This conclusion is supported by the fact that quinoline-3-sulphonic acid and quinoline-1-sulphonic acid both give this tribromoquinoline when they are brominated, for it is known that the first bromine atom enters into the 4′-position. It is to be noted that Claus and Küttner (Abstr., 1887, 278) were not working with pure quinoline-1-sulphonic acid when they obtained a tribromoquinoline of melting point 198°, but with a mixture of this and quinoline-4-sulphonic acid, which by their method yielded only 3 : 4 : 4′-tribromoquinoline; that the tribromoquinoline obtained by Claus and Zuschlag (Abstr., 1890, 267), melting at 185°, is a mixture of 1 : 3 : 4′- and 3 : 4 : 4′-tribromoquinolines; and that Lubavin's (*Beilstein*, **3**, 749) tribromoquinoline (m. p. 173—175°) is impure 1 : 3 : 4′-tribromoquinoline.

1 : 4 : 4′-*Tribromoquinoline* is obtained by heating the hydrobromide dibromide of 1 : 4-dibromoquinoline (m. p. 127°, Abstr., 1890, 172), and fractionally precipitating the acetic acid solution of the residue by the method already given. It forms small needles when crystallised and large needles when sublimed; it melts at 168—168·5° (uncorr.), and dissolves in most organic solvents. Its salts with the stronger mineral acids crystallise well, but are dissociated by water. The *platinochloride* forms orange-red crystals, which are dissociated by water and alcohol. No methiodide has been obtained. Two *nitro*-derivatives, melting at 197° (uncorr.) and 157° (uncorr.) respectively, and soluble and insoluble in alcohol, respectively, have been obtained. This tribromoquinoline is also obtained by brominating 4 : 1-bromoquinolinesulphonic acid (Abstr., 1890, 267); if too much bromine (above 2 mols.) is used, a tetrabromoquinoline melting at 198° is also formed, and the constitution of this is evidently 1 : 3 : 4 : 4′-*tetrabromoquinoline*. It is identical with the tetrabromoquinoline obtained by Claus and Welter (Abstr., 1890, 1320), and is perhaps the compound (m. p. 198°) obtained by Claus and Küttner, and described by them as a tribromoquinoline (see above).

Claus and Posselt (Abstr., 1890, 522) studied the action of phosphorus pentabromide on 1 : 4-hydroxyquinolinesulphonic acid at 130° and 160°, and obtained substances which they described as a bromoquinolinesulphonic bromide and a tribromoquinoline, respectively. Closer investigation has now shown that both these substances still contain the hydroxyl group, being 1-hydroxy-? : 4-bromoquinolinesulphonic bromide and 1-hydroxy-3 : 4 : 4′-tribromoquinoline respectively, and not the aforesaid compounds.

1-*hydroxy*-3 : 4 : 4′-*tribromoquinoline* crystallises in long, brilliant, lustrous, colourless needles, and melts at 172—173°, not 168°; its basic properties are inappreciable, for it forms no platinochloride or methiodide, but yields metallic derivatives with the alkalis and the heavy metals.

When 1-hydroxy-? : 4-bromoquinolinesulphonic acid is treated with tin and hydrochloric acid, the hydroxyl group is reduced, and the hydroquinoline-4-sulphonic acid, $C_9NH_{10}\cdot SO_3H$, described by Lellmann, is obtained; it crystallises with 1 mol. H_2O, and melts at 315° (uncorr.); its *potassium salt* was obtained. A. G. B.

2′-Quinolylacetaldehyde. By E. Carlier and A. Einhorn (*Ber.*, **23**, 2894—2897).—2′-Quinolylacetaldehyde may be prepared by the electrolysis of 2′-quinolyl-α-hydroxypropionic acid, or by the action of concentrated sulphuric acid. On treating quinolylhydroxypropionic acid with a glacial acetic acid solution of bromine, *dibromoquinolylacetaldehyde* is formed, melting at 180°. The *phenylhydrazone* crystallises from alcohol in prisms which melt at 168—169°. The *oxime* crystallises in white needles melting at 235—237°. By the action of phosphorus pentachloride on the aldehyde, 2′-*ω-dichloroethylquinoline*, $C_9NH_6\cdot CH_2\cdot CHCl_2$, is formed, crystallising from ether or alcohol in white needles which melt at 80°.

2′-3′-*Diquinolyl* is prepared from orthamidobenzaldehyde and quinolylacetaldehyde; it crystallises from alcohol in white plates, melting at 175·5°, and is identical with the compound obtained by Weidel by the action of sodium on quinoline.

2′-*Quinolylacetic acid* is formed by the oxidation of the aldehyde, or by fusion with potassium hydroxide; it crystallises from alcohol in white needles which melt at 275°, and may be sublimed without decomposition. The *hydrochloride* melts at 243°. The *calcium salt* forms a white, crystalline powder; the *silver salt* decomposes on exposure to light, and yields quinaldine on distillation in an atmosphere of hydrogen; it is also formed by heating the calcium salt with calcium oxide.

2′-*Quinolylpropionic acid*, $C_9N{\cdot}H_6{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is prepared by the reduction of quinolylacrylic acid with sodium amalgam; it crystallises from water or alcohol in needles which melt at 115—116°. The *ethyl salt* crystallises from light petroleum in needles which melt at 116°. No other salts could be obtained.

2′-*Quinolyldibromopropionic acid*, $C_9NH_6{\cdot}CHBr{\cdot}CHBr{\cdot}COOH$, is formed by the action of bromine on quinolylacrylic acid; it crystallises from glacial acetic acid in white prisms which melt at 180—181°. If this compound is dissolved in an alkaline carbonate solution, and distilled in a current of steam, 2′-*quinolylacetylene*, $C_9NH_6{\cdot}C{\vdots}CH$, is formed; this is an oily liquid, and yields 2′-*quinolyldibromethylene*, $C_9NH_6{\cdot}CBr{:}CHBr$, which is deposited from ether in nodular crystals melting at 63—64°. By the action of excess of bromine on this compound, a *perbromide* is obtained, which crystallises in prisms, and melts at 195—196°.

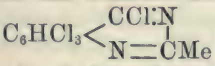
2′-*Quinolyldihydroxypropionic acid*, $C_9NH_6{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH$, is prepared by the oxidation of quinolylacrylic acid with a dilute solution of potassium permanganate at low temperatures; it crystallises from water or alcohol in prisms which melt at 113°; the ethyl salt forms prisms melting at 110·5°. J. B. T.

Nitro- and Chloro-derivatives of β-Methyl-δ-oxyquinazoline (Anhydroacetylorthamidobenzamide). By L. H. Dehoff (*J. pr. Chem.* [2], **42**, 346—360; compare Abstr., 1887, 1043).—*Nitro-β-methyl-δ-oxyquinazoline* is obtained by nitrating β-methyl-δ-oxyquinazoline with nitric acid (sp. gr. 1·5) at the boiling point, and evaporating. It crystallises from hot water as a white powder; it begins to darken at 230°, but is not further changed till 280°; when heated on platinum foil, it explodes feebly; it dissolves in aqueous alcohol and alkalis, but not in ether or benzene. Its solution in ammonia gives a white *silver compound* when precipitated with silver nitrate, but is not precipitated by the salts of other heavy metals. It crystallises unchanged from hot strong hydrochloric acid. The *methyl compound* forms small, slender, white needles melting at 165°.

No monochloro-derivative has been obtained.

Tetrachloro-β-methyl-δ-oxyquinazoline is produced by mixing the oxyquinazoline (8 grams) with phosphoric chloride (25 grams), dissolving the mixture in phosphorous chloride (10 grams), and heating for 12 hours at 170°; the excess of the phosphorus chlorides is distilled off, and the residue washed with soda solution, and crystallised from alcohol; the yield is 53 per cent. It crystallises in white needles which melt at 124—125°, and are insoluble in water, but soluble in most other solvents.

When the tetrachloro-derivative is evaporated with alcoholic potash, and the residue dissolved in water, filtered, and treated with dilute sulphuric acid, a precipitate is obtained which crystallises from alcohol in yellowish prisms melting at 206—207°; the formula of this substance is $C_9H_4Cl_3N_2{\cdot}OH$. The *ethyl* compound, $C_9H_4Cl_3N_2{\cdot}OEt$, is obtained at the same time, being left undissolved by the water; it crystallises from alcohol in soft, lustrous, white needles melting at 75—76°. The *amide*, $C_9H_4Cl_3N_2{\cdot}NH_2$, is obtained by heating the tetrachloro-derivative with alcoholic ammonia at 150—160° for 2—3 hours; the reaction mass is washed with water, and heated with alcohol and animal charcoal; the alcoholic solution is then precipitated with water. The amide crystallises in needles which blacken at 178°, and melt at 183—184°; it dissolves in dilute alcohol and benzene, but not in ether, light petroleum, or water; its *hydrochloride* blackens and decomposes about 200°. A *methylamine* derivative, $C_9H_4Cl_3N_2{\cdot}NHMe$, was obtained by heating the tetrachloro-derivative with methylamine at 110°; it forms white, microscopic needles (with 1 mol. H_2O), which soften at 149°, and melt at 155°. An *anilide*, $C_9H_4Cl_3N_2{\cdot}NHPh$, was also obtained; it crystallises (with 1 mol. alcohol) in thick, white, rhombic tables.

A consideration of the above compounds leads to the conclusion that tetrachloro-β-methyl-δ-oxyquinazoline contains one atom of chlorine situated differently from the other three, and as this atom is easily replaced, it cannot be in the benzene nucleus; the author, therefore, ascribes the formula  $C_6HCl_3<\begin{matrix}CCl{:}N\\ \quad\ |\\ N{=}CMe\end{matrix}$ to the tetrachloro-derivative. The above-described ethyl and amido-compounds will thus be trichloro-β-methyl-δ-ethoxyquinazoline and trichloro-β-methyl-δ-amidoquinazoline, respectively. It is, however, still an open question whether β-methyl-δ-oxyquinazoline is really a hydroxy- or an oxy-derivative (Abstr., 1887, 1043). When the tetrachloro-derivative is reduced with hydriodic acid, β-methyl-δ-oxyquinazoline is obtained; β-methylquinazoline is probably formed, but oxidises at once to the oxy-compound. A. G. B.

Papaveroline. By K. Krauss (*Monatsh.*, **11**, 350—362; compare Abstr., 1889, 166, 167; 1887, 1116).—The hydriodide of this base has been prepared by Goldschmiedt by the action of concentrated hydriodic acid on papaverine, in presence of amorphous phosphorus. When a solution of sodium hydrogen carbonate, saturated with carbonic anhydride, is added to the hydriodide, the free base, $C_{16}H_{13}NO_4,2H_2O$, is precipitated as an almost colourless, crystalline powder, which, when dried in a vacuum, is perfectly stable, and contains 2 mols. H_2O, which are given up at 100°. Heated to 150°, it darkens in colour, and, on raising the temperature to 210°, becomes quite black, without having previously melted. The base dissolves readily in mineral acids, in oxalic acid, and in alcohol, and is very soluble in acetic acid and in glycerol. Dilute potash turns an alcoholic solution blue; strong potash produces a dark-violet coloration.

The hydrochloride, $C_{16}H_{13}NO_4,HCl + H_2O$, crystallises in white needles, soluble in hot water; the sulphate, $(C_{16}H_{13}NO_4)_2,H_2SO_4 + 8\frac{1}{2}H_2O$, is only slightly soluble in water; the oxalate,

$$(C_{16}H_{13}NO_4)_2,C_2H_2O_4 + 3H_2O,$$

crystallises from water in spherical aggregates of needles.

On distillation with zinc-dust in a stream of hydrogen, the author expected to obtain α-benzylisoquinoline. Instead of this, dibenzyldiisoquinoline, $(C_{16}H_{12}N)_2$, and α-methylisoquinoline were formed. The former is insoluble in dilute hydrochloric acid, dissolves readily in ether, light petroleum, acetic acid, and benzene, and when crystallised from alcohol, melts constantly at 234—235°; the latter is an oil, which dissolves in dilute hydrochloric acid, and furnishes a platinochloride, $(C_{10}H_9N)_2,H_2PtCl_6 + 1\frac{1}{2}H_2O$, which, after recrystallisation from water, melts at 229°, and a crystalline picrate which commences to sinter at 198°, and melts at 209—210°. G. T. M.

Strychnine. By C. STOEHR (*J. pr. Chem.* [2], **42**, 399—415).—Most of the analyses of strychnine which have been made agree with the formula $C_{21}H_{22}N_2O_2$. The author has prepared and analysed strychnine hydrochloride (with $1\frac{1}{2}$ mols. H_2O), of which he gives crystallographical measurements, and its platinochloride; also strychnine hydrobromide (with 1 mol. H_2O) and hydriodide (with 1 mol. H_2O); his analyses confirm the above formula for strychnine and the generally accepted formulæ for these salts. Pure commercial strychnine melted at 265—266°; by converting this into the hydrochloride, reconverting the latter into strychnine, crystallising from alcohol, and pulverising the crystals, a light powder was obtained which darkened at 260°, and was a dark brownish-yellow liquid at 269°. Claus and Glassner give the melting point of strychnine as 284° (Abstr., 1881, 747); Beckurts as 285° (uncorr., Abstr., 1885, 675); Loebish and Schoop as 268° (*Monatsh.*, **6**, 858); Beckurts as 265° (Abstr., 1890, 1328); and Garzarolli-Thurnlackh as 262° (*Monatsh.*, **10**, 1).

The author has again investigated the distillation of strychnine with lime (compare Abstr., 1887, 604, 682; 1888, 63), and has again found that hydrogen, ethylene, ammonia, ethylamine, scatole, β-picoline, and, probably, ethylpyridine are produced. As the β-picoline thus obtained seems to be identical with that obtained from other sources, it may be allowed that all β-picolines at present known are identical, whatever their source (compare Ladenburg, Abstr., 1890, 1432).

To obtain trichlorostrychnine (Abstr., 1887, 604) dry, powdered strychnine hydrochloride is heated with phosphoric chloride (4—5 parts) and chloroform in a reflux apparatus on the water-bath as long as hydrogen chloride is evolved; water is then added, and the chloroform distilled off; ammonia is added, the liquid extracted with ether, and the ether residue crystallised from alcohol containing hydrochloric acid. It gives much the same reaction as strychnine with potassium dichromate and sulphuric acid, and a similar colour with nitric and sulphuric acids.

When an excess of phosphoric chloride (7—8 parts) is used, a higher chlorinated derivative is obtained; after distilling off the chloroform, an insoluble mass is left which is extracted with benzene. This derivative crystallises in long, slender, colourless needles when absolute alcohol is added to the hot benzene solution; its composition is in approximate agreement with a pentachlorostrychnine; it darkens and melts at 224°; it does not give the same reaction as trichlorostrychnine with nitric and sulphuric acids. A. G. B.

Brucine. By L. BEREND and C. STOEHR (*J. pr. Chem.*, **42**, 415—420).—De Coninck (Abstr., 1882, 739) distilled brucine with potash, but obtained no homologues lower than lutidine.

The gaseous products of the distillation of brucine with slaked lime were hydrogen, ammonia, and ethylene. The distillate was at first a colourless liquid with a yellow oil suspended in it, but it rapidly became brownish-red in air; it was acidified with hydrochloric acid and distilled in steam, whereby a few drops of scatole were obtained, but the bulk of the liquid did not distil. The liquid was shaken with ether, and then solid potash was added to it until all the oily bases had separated; these were then dissolved in ether. The aqueous liquid contained ammonia and methylamine, while the bases in the ethereal solution were found to be mainly β-picoline and a lutidine, probably β-ethylpyridine, together with smaller quantities of other pyridine bases; quinoline bases were absent. The β-picoline boiled at 142—143°, and was identical with that obtained from strychnine (previous abstract); its sp. gr. at 0°/4° was 0·9756 (Zanoni, 0·9771). A. G. B.

Alkaloïds of Veratrum album. By C. PEHKSCHEN (*J. Pharm.* [5], **22**, 265—269; from *Pharm. Zeit. Russ.*, **29**, 339).—The rhizome of the wild plant gives 0·57 to 0·66 per cent. of mixed alkaloïds, whilst the cultivated rhizome yields only 0·29 per cent. The powdered root is macerated with alcohol during six days at the ordinary temperature, and this repeated a second and third time, the last time with the addition of acetic acid. The first alcoholic extract is faintly acid from the presence of jervic acid. The alcoholic solutions are united, and the major portion of the alcohol is removed by distillation under reduced pressure; on the addition of 3 to 4 vols. of boiling water, resinous substances are precipitated, which are removed by filtration. The remaining resinous and colouring matters are removed by agitation with ether. Hydrogen sodium carbonate is then added to alkaline reaction, then ether, and subsequently chloroform. When the ether and chloroform solutions are evaporated, the mixed alkaloïds are left, and these on being treated with absolute ether, give veratroïdine and a minute amount of jervine in solution, whilst the insoluble portion contains jervine and a third alkaloïd, pseudojervine. *Veratroïdine*, $C_{32}H_{53}NO_9$, melts about 149°, and chars about 172°. It is optically inactive. At 22·5°, 1 part dissolves in 13 parts of benzene, 5·9 of chloroform, and 9·09 of absolute ether. It dissolves in alcohol in almost all proportions. Veratroïdine yields amorphous salts with hydrochloric, hydrobromic, sulphuric, nitric, oxalic, and acetic acids. Most of the general reagents for alkaloïds give with this base more or less of a precipitate, according to the state of concentration. A hydrochloric solution of 1 : 5000 gives a faint turbidity with mercury potassium iodide, and a solution of 1 : 3500 a turbidity with phosphomolybdic acid. With concentrated sulphuric acid, veratroïdine gives a yellow liquid which passes through orange-red to cherry-red, with a green fluorescence, whilst concentrated nitric acid produces a transient rose colour which soon passes to citron-yellow. Hydrochloric acid (11·0 per cent. is best) gives a beautiful rose coloration; this serves to distinguish veratroïdine from veratrine. Veratroïdine, when heated at 120° with ethyl iodide in a sealed tube for 40 hours, yields the compound $C_{32}H_{53}NO_9,2EtI$. *Pseudojervine*, $C_{29}H_{49}NO_{12}$, forms large, rhombic crystals. The root does not contain more than 0·006 per cent. The alkaloïd begins to turn yellow at 215°, and melts at 259° with blackening. It is optically inactive. At 22°, 1 part of this base dissolves in 10·876 parts of light petroleum, in 372 parts of benzene, 1021 parts of absolute ether, 4·1 of chloroform, and 184·8 of absolute alcohol. With phosphomolybdic acid, a solution of 1 : 10,000 gives a perceptible turbidity; but with mercury potassium iodide, the dilution should not exceed 1 : 6000. The pure base gives no colour with either hydrochloric, nitric, or sulphuric acids, the latter mixed with sugar or with other reagent. When mixed with minute quantities of jervine, it gives the coloration reactions described as characteristic of it by Wright and Luff. *Jervine*, $C_{14}H_{22}NO_2$, crystallises from a boiling alcoholic solution in beautiful white needles. It melts at 237·7°, and is slightly lævorotary. At 25°, 1 part of the base dissolves in 1658 parts of benzene, in 268 parts of absolute ether, in 60 of chloroform, and 16·8 parts of absolute alcohol. The base is insoluble in light petroleum, and very slightly soluble in ethyl acetate, water, and carbon bisulphide. Beautiful rhombic crystals of the normal hydrochloride, with 2 mols. H_2O, are obtained by mixing an alcoholic solution of the base with an alcoholic solution of hydrogen chloride; sulphuric acid gives an acid salt under the like conditions. Jervine is characterised by the violet coloration, passing to blue, which it gives with sulphuric acid and sugar; veratroïdine, with this test, gives a brown coloration.

J. T.

Benzyl Derivatives of Piperidine, Tetrahydroquinoline, and Pyridine. A New Method of Formation of Benzyleneimides.

By E. LELLMANN and H. PEKRUN (*Annalen*, **259**, 40—61).—*Paranitrobenzylpiperidine*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_5NH_{10}$, is obtained when piperidine is gradually treated with paranitrobenzyl chloride in well-cooled alcoholic solution, the mixture then boiled for about an hour, and the hydrochloride thus produced decomposed with water. It crystallises from light petroleum in large, amber-coloured plates, melts at 34°, and is very readily soluble in mineral acids and most organic solvents, but only sparingly in water. The *hydrochloride*, $C_{12}H_{16}N_2O_2,HCl$, crystallises from hot alcohol in light-brown prisms, melts at 236°, and is readily soluble in water, but insoluble in ether, benzene, and light petroleum. The *platinochloride*, $(C_{12}H_{16}N_2O_2)_2,H_2PtCl_6$, is a yellow, amorphous, unstable compound.

Paramidobenzylpiperidine, $C_{12}H_{18}N_2$, is formed when the preceding compound is reduced with tin and hydrochloric acid; the product is distilled with steam and recrystallised from hot light petroleum, from which it separates in colourless needles melting at 87°. It is readily soluble in most ordinary solvents except water. The *hydrochloride*, $C_{12}H_{18}N_2,2HCl$, crystallises in yellow needles and is very readily soluble in water.

Dimethylanilineazobenzylpiperidine, $NMe_2·C_6H_4·N_2·C_6H_4·CH_2·C_5NH_{10}$, is produced when a solution of paramidobenzylpiperidine in well-cooled concentrated hydrochloric acid is treated first with sodium nitrite, and then with dimethylaniline. It crystallises from alcohol in golden needles, melts at 109°, and dissolves in dilute acids, yielding a dark-violet solution, the colour of which changes to yellow on the addition of water; it is readily soluble in the ordinary organic solvents, but only sparingly soluble in water. The hydrochloride crystallises from alcohol in small, bluish-black needles, and its aqueous solution imparts to silk and wool a yellow coloration.

Paramidochlorobenzylpiperidine, $NH_3·C_6H_3Cl·CH_2·C_5NH_{10}$, is obtained, mixed, however, with paramidobenzylpiperidine, when the brown light petroleum mother liquors obtained in the purification of the last-named compound are evaporated; it can be purified by converting it into the hydrochloride. It crystallises from light petroleum in colourless needles melting at 76—76·5°. The *hydrochloride*, $C_{12}H_{17}ClN_2,2HCl$, forms yellow, well-defined, transparent crystals.

Orthonitrobenzylpiperidine, $C_{12}H_{16}N_2O_2$, prepared as described in the case of the corresponding para-compound, is a thick, yellow oil having an odour recalling that of piperidine; it is soluble in mineral acids and most ordinary organic solvents. The *hydrochloride*, $C_{12}H_{16}N_2O_2,HCl$, separates from hot alcohol in well-defined, yellowish-green, transparent crystals, sinters together at 124°, and melts completely at 209°. The *platinochloride*, $(C_{12}H_{16}N_2O_2)_2,H_2PtCl_6$, is a yellow, amorphous compound.

Orthamidobenzylpiperidine, $C_{12}H_{18}N_2$, crystallises from hot light petroleum in almost colourless, rhombic plates, melts at 82·5°, and is readily soluble in mineral acids, alcohol, benzene, &c., but more sparingly in water.

Metanitrobenzylpiperidine, $C_{12}H_{16}N_2O_2$, is an oil, and resembles the isomerides described above in its behaviour with solvents. The hydrochloride separates from alcohol in yellow, rhombic crystals. The *platinochloride*, $(C_{12}H_{16}N_2O_2)_2$, H_2PtCl_6, is yellow and amorphous.

Metamidobenzylpiperidine, $C_{12}H_{18}N_2$, crystallises from light petroleum in colourless needles, and melts at 112°.

Paranitrobenzyltetrahydroquinoline, $NO_2·C_6H_4·CH_2·C_3NH_{10}$, can be obtained by heating paranitrobenzyl chloride (1 mol.) with tetrahydroquinoline (2 mols.) for 1 to 2 hours in alcoholic solution, and decomposing the salt thus produced, with water; it crystallises from hot alcohol or ether in long, bright-red prisms melting at 102°. The *platinochloride*, $(C_{16}H_{16}N_2O_2)_2,H_2PtCl_6$, is a sparingly soluble, yellowish-red compound. The corresponding ortho-compound crystallises in brownish-red plates, melts at 111°, and forms a yellow, amorphous *platinochloride*. The meta-*base* crystallises from alcohol in short, red prisms, melts at 99°, and is only moderately easily soluble in ether, cold alcohol, chloroform, and dilute acids. The three nitrobenzyltetrahydroquinolines are only feeble bases, and their hydrochlorides are decomposed by water; they give König's reaction for tetrahydroquinoline with oxidising agents, and on reduction they yield the corresponding amido-compounds, of which the meta-derivative, $NH_2·C_6H_4·CH_2·NC_9H_{10}$, is crystalline, and melts at 82°.

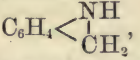
Paranitrobenzylpyridine chloride, $NO_2·C_6H_4·CH_2·C_5NH_5Cl$, is formed when paranitrobenzyl chloride is warmed with excess of pyridine. It crystallises from alcohol in yellow prisms, sinters together at about 90°, melts at about 103°, and is readily soluble in water, alcohol, benzene, and mineral acids, but only very sparingly in ether and light petroleum. The *platinochloride*, $(C_{12}H_{11}N_2O_2Cl)_2,PtCl_4$, crystallises from dilute hydrochloric acid in golden plates, and melts at 220—223° with decomposition.

Paramidobenzylpyridine chloride hydrochloride, $C_{12}H_{13}N_2Cl,HCl$, is obtained in yellow crystals when the nitro-compound is reduced with tin and hydrochloric acid. It melts at 183—185°, decomposes at 200—202°, and is only sparingly soluble in alcohol. When treated with alkalis, it yields a yellowish, resinous compound which does not melt below 280°, and when heated at 210—220° it is decomposed into the hydrochlorides of pyridine and parabenzyleneimide. The *platinochloride*, $(C_{12}H_{13}N_2Cl)_2,H_2PtCl_6$, is crystalline.

Orthonitrobenzylpyridine chloride, $C_{12}H_{11}N_2O_2Cl$, prepared by heating pyridine with orthonitrobenzyl chloride, crystallises from alcohol and ether in yellowish prisms, melts at about 76°, and gradually decomposes at a higher temperature; it resembles the corresponding para-compound in its behaviour with solvents. The *platinochloride*, $(C_{12}H_{11}N_2O_2Cl)_2,PtCl_4$, crystallises in yellow scales.

Orthamidobenzylpyridine chloride hydrochloride, $C_{12}H_{13}N_2Cl,HCl$, is a colourless, semi-crystalline powder, which melts at about 169° and decomposes at a higher temperature, yielding orthobenzyleneimide; the last-named compound is a reddish-brown powder which does not melt below 290°.

Metanitrobenzylpyridine chloride, $C_{12}H_{11}N_2O_2Cl$, crystallises from alcoholic ether in yellow needles, sinters together at 60°, and melts completely at 100°. The *platinochloride*, $(C_{12}H_{11}N_2O_2Cl)_2,PtCl_4$, crystallises in small, yellow needles. *Metamidobenzylpyridine chloride hydrochloride*, $C_{12}H_{13}N_2Cl,HCl$, is a colourless powder which melts at about 220° with decomposition.

Metabenzyleneimide,  $C_6H_4<\begin{matrix}NH\\ |\\ CH_2\end{matrix}$, is obtained, together with pyridine hydrochloride, when the preceding compound is heated at 230°; it is a yellow, amorphous powder melting at 120—145°. The *platinochloride* has the composition $(C_7H_7N)_2,H_2PtCl_6$. Molecular weight determinations by Raoult's method gave results which showed that parabenzyleneimide is probably a polymeride of a compound of the molecular formula C_7H_7N. F. S. K.

Tropidine. By A. EINHORN (*Ber.*, **23**, 2889—2894).—By the action of aqueous hypochlorous acid on tropidine, two compounds are formed, and may be separated by recrystallisation from dilute alcohol; the one is deposited in long, lustrous prisms which melt at 138°; the second is more soluble, separates in white, nodular crystals melting at 108—109°, and has the formula $C_8H_{13}N_2HOCl$.

On heating tropidine with a glacial acetic acid solution of hydrobromic acid in a sealed tube at 100°, the salts of two isomeric hydrobromotropidine hydrobromides are formed, and may be separated by crystallisation from alcohol; the more insoluble is termed the α-compound, and the second the β-compound. *α-Hydrobromotropidine hydrobromide*, $C_8H_{14}NBr,HBr$, is obtained as the chief product if the heating is continued for 70 hours; it is very soluble in water, and crystallises in transparent prisms which melt at 219—220°. The *free base* is liberated by the action of aqueous soda. *β-Hydrobromotropidine hydrobromide*, $C_8H_{14}NBr,HBr + H_2O$, is formed if the reaction is allowed to proceed for only 24 hours; it crystallises from alcohol in lustrous, prismatic needles melting at 113—114°; on heating to 105°, the anhydrous compound is obtained, which differs, however, from the α-derivative. The *free base* is formed by the action of alkalis; on treating it first with anhydrous sodium acetate and then with aqueous soda, a small quantity of a base is obtained which yields a *platinochloride* melting at 200°; tropine platinochloride melts at the same temperature. The author suggests that the compound prepared by Ladenburg (compare Abstr., 1890, 1167), by the action of hydrobromic acid on tropidine at low temperatures, is really identical with β-hydrobromotropidine.

Tropidine dibromide, $C_8H_{13}NBr_2$, is prepared by treating a glacial acetic acid solution of tropidine with excess of bromine dissolved in the same medium; the oil which separates is washed with sulphurous acid; on the addition of potassium carbonate, the dibromide separates. On adding water to the alcoholic solution, it crystallises out in small, lustrous plates which melt at 66—67·5° with previous softening. On boiling the dibromide with dilute sodium hydroxide solution, a penetrating, aromatic odour is produced which greatly resembles that of dihydrobenzaldehyde (compare this vol., p. 67). J. B. T.

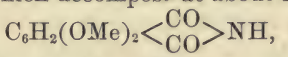
Aconitine. By A. LUBBE (*Chem. Centr.*, 1890, ii, 148—149; from *Apoth. Zeit.*, 5, 321).—From the tubers of the Japanese plant Kusauzu, the author has extracted, by means of Duquesnel's method, an alkaloïd of the formula $C_{33}H_{44}NO_{12}$, which he considers to be identical with the alkaloïd obtained from *Aconitum napellus*. Wright's formula for aconitine is $C_{33}H_{43}NO_{12}$, whilst that of Jürgens is $C_{33}H_{47}NO_{12}$.

Aconitine forms radially fibrous groups of crystals of the rhombic system. The crystals measured by the author had the following faces:—Obtained from the cold saturated solution, $\infty\breve{P}\infty$, ∞P, $0P$; from the hot saturated solution, ∞P, $\infty\breve{P}\infty$, $0P$, $\breve{P}\infty$, P. At 110°, it is partially decomposed; it melts at 183—184°; $[\alpha]_D$, −34·46. The taste is not bitter, but prickly and burning. The most delicate reagents for aconitine are hydrogen iodide and potassium mercury iodide. The hydriodide, even when present in very small quantity (0·02 milligram), appears crystalline under the microscope. Pseudoaconitine could not be detected. The author finds that aconitine has the same physiological properties as are ascribed to it by Lewins, acting on the extremities of certain nerves. It does not appear itself to undergo any change, nor does it in any way decompose the blood corpuscles.

From the tubers of Langaard's variety, "Shirakawauzuware" of *Aconitum sinense*, the author obtained 0·02 per cent. of a crystalline alkaloïd and two amorphous bases. He considers the alkaloïd to be identical with aconitine from *Aconitum napellus*; it melts at 180·9°. Pseudoaconitine could not be detected. J. W. L.

Hydrastine. By M. Freund and M. Heim (*Ber.*, **23**, 2897—2910).—It has previously been shown (Abstr., 1890, 532) that alkylhydrastines are formed by the action of alkalis on the additive compounds of hydrastine and alkyl haloïds; aqueous ammonia reacts in a similar manner in the cold, but on boiling an alcoholic solution of hydrastine methiodide with concentrated aqueous ammonia, a compound is obtained crystallising from alcohol in white, strongly refractive, rhombic plates which melt at 180°, are almost insoluble in water, and dissolve sparingly in ether, carbon bisulphide, or benzene. The substance is a powerful base, and decomposes ammonium salts; it has the formula $C_{22}H_{26}N_2O_6$, and the author proposes to term it *methylhydrastamide*. It may also be obtained by the action of ammonia on methylhydrastine. The salts of the amide are somewhat difficult to prepare, as they readily part with the elements of water. The *picrate* crystallises from alcohol in small, yellow needles. The *hydrochloride*, $C_{22}H_{26}N_2O_6,HCl + 2H_2O$, is deposited in white needles which melt at 116—118°.

Methylhydrastimide, $C_{22}H_{24}N_2O_5$, is prepared by the action of dilute acids, or of concentrated potassium hydroxide solution, on the amide; it crystallises from alcohol in slender, light-yellow needles which melt at 192°, and are insoluble in water. The *hydrochloride*, $C_{22}H_{24}N_2O_5,HCl$, crystallises from absolute alcohol in slightly yellow needles which melt at 227°; a hydrated salt melting at 110—120° may also be obtained. The *platinochloride* crystallises from hydrochloric acid in brown rhombohedra melting at 205° with decomposition. The *sulphate* is deposited from alcohol in yellow crystals which melt at 218°. The *nitrate*, $C_{22}H_{24}N_2O_3,HNO_3 + H_2O$, crystallises in slender needles which decompose at about 230°.

Hemipinimide,  $C_6H_2(OMe)_2{<}\substack{CO\\CO}{>}NH$, is formed by the oxidation of methylhydrastamide with dilute nitric acid.

Ethylhydrastamide, $C_{23}H_{28}N_2O_6$, is prepared by the action of ammonia on hydrastine ethiodide, and is more readily soluble in alcohol than the methyl derivative; it crystallises in rhombic plates which melt at 140°.

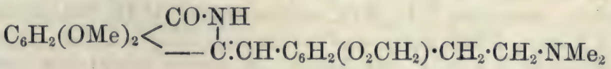
Ethylhydrastimide, $C_{23}H_{24}N_2O_5$, is obtained on treating the amide with dilute acids; it crystallises from alcohol in rhombohedra which melt at 150—151°.

Methylhydrastimide methiodide, $C_{22}H_{24}N_2O_5,MeI + 1\frac{1}{2}H_2O$, is formed by the action of methyl iodide on methylhydrastamide or methylhydrastimide; it crystallises from water in yellow, flat rhombohedra which melt at 240—245°.

The action of amines on the additive compounds of hydrastine and alkyl haloïds is strictly analogous to that of ammonia itself. *Methylhydrastomethylamide*, $C_{23}H_{28}N_2O_6$, is prepared by heating hydrastine methiodide with an alcoholic solution of methylamine in a sealed tube at 100°; it crystallises from alcohol in white rhombohedra melting at 182°, and is not acted on by concentrated aqueous potash. The *hydrochloride* crystallises from alcohol in white needles which melt at 193°. Hemipinomethylimide is formed by the oxidation of the base with dilute nitric acid. *Methylhydrastethylamide*, $C_{24}H_{30}N_2O_6$, is obtained by digesting hydrastine methiodide with an alcoholic solution of ethylamine for several days; it forms white crystals which melt at 162°, and yields hemipinethylimide on oxidation. *Methylhydrastisoamylamide*, $C_{27}H_{36}N_2O_6$, is deposited from alcohol in long, slender crystals which melt at 171°. On heating this compound with a large excess of dilute hydrochloric acid, *methylhydrastisoamylimide* is formed as an oily liquid; the *platinochloride* is a yellow, crystalline powder. *Methylhydrastallylamide*, $C_{25}H_{30}N_2O_6$, crystallises from alcohol, and melts at 158°. By the action of dilute hydrochloric acid, the corresponding *imide* is obtained as a viscid liquid which yields a crystalline *platinochloride*. In the authors' opinion, the above results all tend to confirm the second of the formulæ proposed for methylhydrastine (*loc. cit.*); the action of ammonia on methylhydrastine is therefore represented as being strictly analogous to its action on benzylidenephthalide; methylhydrastamide and methylhydrastimide would consequently be represented by the formulæ

$$NMe_2\cdot CH_2\cdot CH_2\cdot C_6H_2(O_2CH_2)\cdot CH_2\cdot CO\cdot C_6H_2(OMe)_2CO\cdot NH_2$$

$$[CH_2 : H_2 : CH_2 = 1 : 4 : 5 : 6;\ (OMe)_2 : CONH_2 : CO = 1 : 2 : 3 : 4]$$

and 

$$C_6H_2(OMe)_2{<}\begin{array}{l}CO\cdot NH\\ \qquad\ |\\ —C{:}CH\cdot C_6H_2(O_2CH_2)\cdot CH_2\cdot CH_2\cdot NMe_2\end{array}$$

respectively.

J. B. T.

Hydrastine. By .M Freund and A. Philips (*Ber.*, **23**, 2910—2917; compare preceding abstract).—*Hydrastine allyl iodide*,

$$C_{21}H_{21}NO_6,C_3H_5I,$$

is prepared by treating an alcoholic solution of hydrastine with excess of allyl iodide; it crystallises from water or dilute alcohol in small, white needles which melt at 193°. By the action of potassium hydroxide (1 mol.) on this compound, *allylhydrastine*, $C_{24}H_{25}NO_6$, is formed, crystallising from alcohol and ether in deep-yellow needles which melt at 116°. *Allylhydrasteïne*, $C_{24}H_{27}NO_7 + 1\frac{1}{2}H_2O$, is prepared by boiling allylhydrastine with concentrated aqueous potash, and is deposited from water in white crystals which melt at 136°. *Allylhydrastamide*, $C_{24}H_{28}N_2O_6$, is formed by the prolonged action of aqueous ammonia on an alcoholic solution of hydrastine allyl iodide; it may be recrystallised from dilute alcohol, and melts at 156°. *Allylhydrastimide*, $C_{24}H_{26}N_2O_5$, is prepared by the action of dilute acids, or of concentrated aqueous potash, on the amide; it is deposited from dilute alcohol in pale-yellow crystals which melt at 139°. The *hydrochloride* is obtained from alcohol in pale-yellow crystals melting at 211°. The *sulphate* crystallises from dilute alcohol in small, deep-yellow, slender needles which melt at 235°. *Allylhydrastimide allyl iodide*, $C_{27}H_{31}N_2O_5I$, is formed by the action of allyl iodide on allylhydrastamide or allylhydrastimide; it crystallises from dilute alcohol, and melts at 207°. On boiling this compound with concentrated aqueous potash, diallylamine is eliminated, and a substance of the formula $C_{20}H_{17}NO_5$ is formed, to which it is proposed to apply the term *hydrastophthalimidine;* it is deposited in deep-yellow crystals which melt at 226°, and is strictly analogous to the compounds previously described (*loc. cit.*). *Dibromohydrastophthalimidine*, $C_{20}H_{17}NO_5Br_2$, is prepared by treating the preceding compound with bromine (2 mols.); and on the addition of light petroleum to its benzene solution, it crystallises in pale-yellow plates melting at 158°.

The constitution of the above compounds corresponds with that of the derivatives previously described (*loc. cit.*). J. B. T.

Hydrobromanhydroecgonine. By A. EICHENGRÜN and A. EINHORN (*Ber.*, **23**, 2888).—Anhydroecgonine hydrochloride is heated at 100° for 6—7 days with five parts of a solution of hydrogen bromide in glacial acetic acid, saturated at 0°. The product is allowed to crystallise, and the crystals treated with hot water; on cooling, *hydrobromanhydroecgonine hydrobromide*, $C_9H_{14}NO_2Br,HBr$, is deposited in strongly refractive prisms which melt at 250° with decomposition, and are very sparingly soluble in water, alcohol, or glacial acetic acid. J. B. T.

Alkaloïds of the Areca Nut. By E. JAHNS (*Ber.* **23**, 2972—2978).—The author has previously described the preparation of the two alkaloïds, *arecoline*, $C_8H_{13}NO_2$, and *arecaïne*, $C_7H_{11}NO_2$, from the areca nut (Abstr., 1889, 420), and mentioned also a third substance, obtained in small quantity, the nature of which could not then be ascertained. Further investigation has shown that this compound is choline, which was identified by its *platinochloride.* The latter crystallises from water in orange-red, anhydrous, monosymmetric plates, and not as stated by Hundeshagen (*J. pr. Chem.* [2], **28**, 246), in rhombic crystals. The statement of the latter, that the platinochloride crystallises from dilute alcohol in anhydrous, yellow octahedra is also partially incorrect, as the crystals thus obtained contain 1 mol. H_2O. The anhydrous compound melts with evolution of gas at 225°. *Choline aurochloride* melts at 244—245°.

When arecoline is heated in a sealed tube with hydrochloric acid, or boiled with hydriodic acid, potash, or baryta-water, a methyl group is eliminated, and a new compound having the composition $C_7H_{11}NO_2$ obtained. This is isomeric with arecaïne, and may therefore be termed *arecaïdine.* It is most readily prepared by means of baryta-water or hydriodic acid, and crystallises from 60—70 per cent. alcohol in colourless, four- or six-sided plates which contain 1 mol. H_2O. It loses the latter at 100°, and then melts with evolution of gas at 222—223°, and carbonises on further heating. It is readily soluble in water and dilute alcohol, almost insoluble in absolute alcohol, ether, chloroform, and benzene. Its solution is coloured red by a trace of ferric chloride, and, like arecaïne, which it closely resembles in other respects, it is not poisonous.

Its *platinochloride*, $(C_7H_{11}NO_2)_2,H_2PtCl_6$, crystallises in yellow octohedra which melt at 208—209° with evolution of gas, and the *aurochloride*, $C_7H_{11}NO_2,HAuCl_4$, forms four-sided prisms which melt at 197—198°.

If finely divided arecaïdine be suspended in methyl alcohol, and the latter saturated with hydrogen chloride, arecoline is re-formed. If ethyl alcohol be substituted for methyl alcohol, *arecaïdine ethyl ether*, or *homarecoline*, $C_9H_{15}NO_2$, is obtained; this is a colourless, strongly alkaline liquid, miscible with water, alcohol, and ether, distils without decomposition, is volatile with steam, and has poisonous properties very similar to those of arecoline. Its *hydrochloride* crystallises in very hygroscopic needles which deliquesce in the air. The other salts are also deliquescent, and cannot be obtained in crystals. The *picrate* is an amorphous resinous mass, and the *aurochloride* an oily liquid, sparingly soluble in cold, readily in hot water. The *platinochloride* forms an orange-red, amorphous mass which has the composition $(C_9H_{15}NO_2)_2,H_2PtCl_6$, and commences to decompose at 100°.

The above reactions show that arecaïdine is a monobasic acid, and that both oxygen atoms are present as carboxyl. This is confirmed by the fact that no acetyl derivatives of arecaïdine can be obtained, which should be readily formed if the oxygen were present as hydroxyl. The formula for arecoline may therefore be partially resolved into $C_6H_{10}N\cdot COOMe$. Experiments to determine the composition of the group $C_6H_{10}N$ are now in progress. H. G. C.

Action of Sulphurous Anhydride on Flour. By — BALLAND (*J. Pharm.* [5], **22**, 241—244).—The gluten of flour which has been acted on by sulphurous anhydride loses its cohesion, so that, in place of 28—30 per cent., not more than 6 or 7 per cent. can be obtained by the ordinary process of washing, the remainder passing away with the wash water. The gluten is simply modified, not destroyed, as the flour retains its nutritive properties. Sulphuric and sulphurous acids, and alkaline sulphides, all affect gluten in this way, whilst certain compounds, such as sodium chloride, alum, and copper sulphate, favour the aggregation of gluten. Perfectly sound and good bread can be made from the sulphurised flour by mixing with fresh flour and increasing the proportion of salt and yeast. Biscuit made from the defective flour is quite good. J. T.

Formation of Carbamide from Albumin. By E. DRECHSEL (*Ber.*, **23**, 3096—3102).—The author has previously shown that a mixture of several bases is obtained by boiling caseïn with concentrated hydrochloric acid and stannous chloride; the nitrate of one of these bases forms with silver nitrate an additive compound of the formula $C_6H_{13}N_3O_2,HNO_3,AgNO_3$, as the salt probably contains a molecule of water of crystallisation; the base, which the author terms *lysatine* or *lysatinine*, is homologous with creatinine or with creatine, and, like the latter, it yields carbamide on boiling with baryta-water. The author points out the physiological importance of his observations, which prove, for the first time, that carbamide may be obtained from albumin by simple hydrolytic processes.

J. B. T.

Physiological Chemistry.

Influence of Bile on Pancreatic Digestion. By S. MARTIN and D. WILLIAMS (*Proc. Roy. Soc.*, **48**, 160—165).—In a previous communication (Abstr., 1888, 618), it has been pointed out that in the pig the presence of bile or bile salts hastens the action of the pancreatic juice on starch. The same holds good for these secretions in oxen and in the human subject. Investigations made with certain constituents of the bile and related substances gave the following results:—Sodium taurocholate hastens the pancreatic digestion of starch; glycocholic acid arrests it; sodium glycocholate acts like the taurocholate; glycocine has no effect; leucine and tyrosine both hinder the digestion to a slight extent; sodium carbonate, when present in the proportion of 0·25 per cent. and over, retards the digestion of starch by pancreatic extract; but this retardation can be, to a certain extent, neutralised by the addition of bile salts.

In another series of experiments, it was found that the power of bile to hasten pancreatic digestion is not limited to amylolytic digestion, but that it is equally, if not more, marked in its influence on proteolytic digestion. This property is due to the bile salts present; the action of the sodium glycocholate was found, however, to be less effective than the bile salts as a whole. W. D. H.

Action of Nicotine on the Heart and Blood-vessels. By E. COLAS (*Compt. rend. Soc. Biol.* [9], **11**, 31—33).—Experiments were made on dogs in which small doses of nicotine, dissolved in water, were injected into the femoral vein. Blood pressure was taken from the carotid artery. At first the pressure falls and the heart beats irregularly; the pressure returns to the normal level, then rises above it; the heart beats are very small and very rapid; it gradually slows, however, till the normal is re-established. This action is considered to be due to the action of the drug on the intracardiac nerve centres; the acceleration is, however, probably due to its action on the cardiac muscle. It was also noted that a rise of venous pressure occurs simultaneously with that in the arterial system. The rise of pressure is probably due to the increased tonicity of the heart, as the drug stimulates the vaso-dilatator nerves, producing increased redness of the organs. W. D. H.

Pigments of the Aplysiæ. By R. SAINT-LOUP (*Compt. rend. Soc. Biol.* [9], **11**, 116—117).—The green pigment of the liver of this marine mollusc can be extracted from the organ by alcohol. The extract has an intense green colour, and shows spectroscopically the bands of chlorophyll. After saponification with lime, ether or chloroform dissolves out a yellow pigment, the residue being green. The origin of the pigment is believed to be the food (Algæ) of the animal. The pigment is absent in young Aplysiæ which had never fed, and gradually diminishes in those allowed to die of starvation.

W. D. H.

Liquids from Hydatid Cysts. By Roeser (*J. Pharm.* [5], **22**, 244—249).—The contents of a cyst, examined in 1888, measured about 1100 c.c. The liquid was slightly opaline, faintly alkaline, and had a sp. gr. of 1·0075. The solid residue of 14·7 grams per litre, on calcination, yielded 9·30 grams of ash which contained—sodium chloride, 6·95 grams; sodium phosphate, carbonate, sulphate, 0·71 gram; calcium phosphate, sulphate, and carbonate, 1·26 grams; iron, magnesia, and loss, 0·38 gram. The organic matter, corresponding with 5·40 grams per litre, consisted of—albumin, precipitated by heat and acetic acid, 1·060 gram; glucose, 0·585; fatty matter, soluble in ether, 0·260; urea, 0·500; colouring matter of bile, peptone, extractives, 2·995 grams. The nature of these extractive substances has not been clearly determined, although the liquids of cysts have been frequently investigated. Numerous authors are quoted to show that the composition of the liquids is extremely variable. J. T.

Lanolin and the Detection of Cholesterin Fats in Man. By O. Liebreich (*Chem. Centr.*, 1890, ii, 149—150; from *Arch. Physiol.*, 1890, 363—365).—In studying the question of the presence of cholesterin and similar fats in the animal epidermis, the author has applied Liebermann's cholestol reaction with acetic anhydride and concentrated sulphuric acid, and also the property which cholesterin fats have of emulsifying with water to the extent of 200 per cent. In this way, cholesterin fats were found on human skin and hair, the feathers and beaks of birds, and the hoofs of horses.

In addition to the Liebermann's test already mentioned, the author has used a modification in which chloroform is used, and which is a much more delicate test.

Further, a separation of the cholesterin fats has been effected by the author, by treating them with hot ethyl acetoacetate or ethyl ethylacetoacetate, which dissolve cholesterin much more freely than lanolin. Lanolin was found in human vernix caseosa.

J. W. L.

Composition of the Milk of Cows during Early and Late Periods of Lactation. By M. Kühn (*Bied. Centr.*, **19**, 622—628; from *Milchzeit.*, **18**, 922—926).—Experiments were made with cows in early and late periods of lactation, in order to determine the difference in the amount and quality of the milk with cows of the same kind, and of about the same weight, under the same conditions as to feeding. The results show that considerably more milk is produced in early than in late periods, but that the milk of the latter contains rather more dry matter, fat and proteïn, than that of the former. The amount of ash and lactic acid is about the same in both cases. In the late period, the amount of dry substance, milk-sugar, and fat, varies more than in the early period, when the reverse was observed, but in less degree, regarding the other constituents.

N. H. J. M.

Elephant's Milk. By C. A. Doremus (*Chem. Centr.*, 1890, ii, 209; from *Meierei. Tidning. Milchztg.*, 1890, 227).—The following analyses have been made:—

	April 5th, morning.	April 9th, midday.	April 10th, morning.
Water	67·567	69·286	66·697
Total solids	32·433	30·713	33 303 ·
Fat	17·546	19·095	22·080
Solids not fat	14·887	11·619	11·233
Caseïn	14·236*	3·694	2·212
Sugar	14·236	7·267	7·392
Mineral matter	0·651	0·658	0·629

The milk has a pleasant taste and smell, and resembles that of the cow; no unpleasant odour is produced on warming it.

J. W. L.

The Passage of Naphthol into the Urine. By E. Desesquelle (*Compt. rend. Soc. Biol.* [9], **11**, 101—104).—Naphthol is sometimes employed as an inunction in cases of psoriasis. After its use it can be detected as such in the urine. The residue of the ethereal extract of urine, dissolved in chloroform, treated with soda and then with sulphuric acid, gives the green coloration described by Gautrelet (*Traité d'analyse urologique*, 1889) as characteristic of naphthol. Its extreme insolubility renders its absorption slow as a rule, and this property also justifies Bouchard's selection of the drug in cases where it is necessary to keep up prolonged antisepsis. W. D. H.

Uro-phosphates and Hippuro-phosphates. By Gaube (*Compt. rend. Soc. Biol.* [9], **11**, 404—405).—The salts of uric and hippuric acids in the urine are considered to be double salts composed of two acids united to the same base, and thus so-called uro-phosphates and hippuro-phosphates of sodium, potassium, calcium, &c., are described.

W. D. H.

Colouring Matter of Yellow Silk and its Relation to Vegetable Carrotene. By R. Dubois (*Compt. rend.*, **111**, 482—483).—Yellow silk contains several colouring matters, those actually isolated being (1) a golden-yellow compound, soluble in potassium carbonate solution, from which it is precipitated in very brilliant plates; (2) macled crystals, reddish-yellow by transmitted light, and brown-red by reflected light; (3) a lemon-yellow, amorphous substance, which separates in rounded granules when its alcoholic solution evaporates spontaneously; (4) lemon-yellow, octahedral crystals, resembling those of sulphur; and (5) a deep greenish-blue pigment, which is probably crystallisable, but which is present only in very small quantity.

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* Evidently the wrong figure has been given here.

The substances 2, 3, and 4 agree in many respects with vegetable carrotene; they are yellowish-red and crystallisable, dissolve in alcohol, ether, chloroform, and benzene, giving golden-yellow solutions, and in carbon bisulphide giving a brownish-red solution; they alter when exposed to air and light, give a continuous absorption spectrum, and dissolve in sulphuric acid with production of a blue coloration which changes to green, and disappears on addition of water.

Yellow silk owes part, at any rate, of its colour to a substance showing very close analogies to the colouring matter recently extracted from *Diaptomus denticornis* by R. Blanchard, who regards it as carrotene of animal origin. C. H. B.

Poisoning by Hydrocyanic Acid applied to the Surface of the Eye. By N. Gréhant (*Compt. rend. Soc. Biol.* [9], **11**, 64—65).—It was demonstrated that the statement of the older writers that an animal may be poisoned by hydrocyanic acid absorbed through the mucous membrane of the eye is quite correct. Dogs or rabbits are killed in this way in the course of a few minutes. The animals were tracheotomised, and care taken that no poisoning took place from fumes of the drug entering the respiratory cavity. W. D. H.

Physiological Action of Potassium Ferrocyanide. By Combemale and Dubiquet (*Compt. rend. Soc. Biol.* [9], **11**, 169—172).—Potassium ferrocyanide is not toxic even when given to animals in doses of 2 grams per kilo. of body weight. In those animals which do not vomit (for instance, the cobaye), there is a diuretic action even after small doses, three hours after its administration. In dogs this is not the case. Repeated doses of the salt, however, cause intestinal troubles in the dog, vomiting being produced if the amount given exceeds 80 centigrams per kilo. of body weight.

In its passage through the system, the ferrocyanide is changed into the ferricyanide, which is eliminated in the urine. Its diuretic action appears to be connected with this transformation, and the simultaneous formation of diuretic potassium salts. W. D. H.

Physiological Action of the Soluble Salts of Strontium. By J. V. Laborde (*Compt. rend. Soc. Biol.* [9], **11**, 453—459).—Strontium appears to be quite innocuous. In the dog, the only noticeable feature after the administration of the chloride is slight diuresis It thus differs from barium salts, which are very toxic, producing cessation of respiration. Soluble salts of potassium, especially the chloride, lactate, and sulphate, are also poisonous, producing emesis and diarrhœa, and in larger doses slowing of the heart and death from asphyxia. Calcium salts, like those of strontium, are apparently harmless. W. D. H.

Physiological Action of Guaiacol. By P. Marfori (*Chem. Centr.*, 1890, ii, 155—156; from *Ann. chim. farm.*, **11**, 304—327).—The physiological value of guaiacol was pointed out by Seidel in 1880, since then one difficulty met with in using it has been the absence of distinctive tests of its purity. The author finds that one part of guaiacol should dissolve in 60 parts of water, the presence of impurities rendering it more soluble. Its boiling point is 200—202°. One drop of pure guaiacol mixed with a few drops of concentrated sulphuric acid gives a beautiful permanent purple-red coloration, which is interfered with by even a trace of impurity.

The general action of guaiacol consists in first exciting and then paralysing the nerve centres. The paralytic effects are the feebler the higher the animal subjected to its influence. In small doses, guaiacol does not affect the pulse, in larger doses it is quickened. The temperature is reduced. After death from the effects of guaiacol, the author has observed, in the case of dogs, that the heart is not affected by electric stimulus, although the other muscles are. Its action is similar to that of phenol or catechol, and it is ejected from the system in a similar condition; it is, however, not so poisonous as these. J. W. L.

Substances which Favour Infection. By G. H. Roger (*Compt. rend. Soc. Biol.* [9], **11**, 307—310).—There are certain materials, such as lactic acid, which, when introduced simultaneously with microbes into an animal, favour the development of the bacteria. The bacillus of symptomatic anthrax is innocuous to the rabbit, but is fatal when there is a simultaneous injection of the materials formed by the activity of certain other micro-organisms (*B. prodigiosus*, *Staplylococcus aureus*, &c.). The substance in the cultures that acts thus is soluble in glycerol but insoluble in alcohol, and therefore resembles the soluble ferments; it is, however, not the same substance which liquefies the gelatin in the culture tubes, as it is not destroyed by a temperature of even 130°. Similar interactions between other bacteria are described; and the fact is thought worthy of note, as it may furnish bacteriologists with a means of re-establishing the virulence of micro-organisms which have become attenuated by prolonged cultivation through the bodies of a long series of animals; and also that it may help to explain why some vegetable poisons like papaïn and jequirity, which are free from microbes, yet produce a condition of the body in which it swarms with numerous bacteria which normally are harmless, or only harmful to a slight degree. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Soluble Ferment of Urea. By P. Miquel (*Compt. rend.*, **111**, 397—399).—The soluble urea ferment described by Musculus has not been isolated by subsequent observers. It can, however, readily be obtained in the following way:—Peptone solution mixed with 2 to 3 grams of ammonium carbonate per litre is sterilised by filtration through porcelain, and is then inoculated with one of the active bacillian ferments of urea, which the author has previously described (*Ann. Micro.*, **1** and **2**). After some days, the liquid becomes turbid, and contains the diastase in question. It is necessary that the cultivations of bacilli be quite pure, for other organisms may develop to the exclusion of the microbes, or may destroy the diastase as fast as it is formed. The quantity of soluble ferment obtained in this way per litre of peptone solution is sufficient to convert 60 to 80 grams of urea into ammonium carbonate in less than an hour. The temperature at which this change takes place most rapidly is 50° to 55°, but even at 50° in contact with air, the diastase undergoes profound alteration, and it is completely destroyed after three or four hours. At a temperature near 0°, however, the solutions of the diastase in the peptone solution can be kept for several weeks without alteration. At 75°, the ferment is completely destroyed in a few minutes, and at 80°, in a few seconds. On the other hand, the organisms which secrete the ferment often resist a moist temperature of 95° for two or three hours.

The author has cultivated 14 species of micro-organisms, exclusive of *Mucedinæ*, which are capable of producing ammoniacal fermentation of urea, and which present perfectly distinct morphological characters, and different degrees of activity. All these microbes secrete the soluble ferment when they are grown in proteïd cultivation fluids free from urea, and the author concludes that the destruction of urea at the ordinary temperature in the absence of chemical reagents is due to the action of this soluble ferment. Urea itself has very little nutritive power for lower organisms, and it would seem that the ammoniacal fermentation of urea is not due directly to an act of nutrition, but that the microbes secrete the soluble ferment, and the latter acts on the urea.

C. H. B.

Nitrification and Denitrification in Soils. By T. LEONE (*Gazzetta*, **20**, 149—151). The author has previously shown (Abstr., 1890, 1453) that the phenomena of nitrification and denitrification in waters are due to the activity of bacteria and occur in alternation, according to the amount of nutriment present; thus, when an abundance of nutritive matter is at hand, the rapid development of the germs is accompanied by the oxidation of the proteïds, partly at the expense of the oxygen in the nitrates present, ammonia and nitrites being formed. On the other hand, nitrification commences as soon as the decomposable azotised products are either assimilated or converted into ammonium compounds. If nitrification and denitrification are determined by similar conditions in soils, the effect of manuring would be in the first instance to suspend the ordinary process of nitrification, and to convert part of the nitrates present into nitrites, nitrification only recommencing when the organic matter was decomposed, and the formation of ammonia had attained a maximum. The following experiments show that this is actually the case.

Two samples, A and B, of 10 kilos. each, of garden mould were placed in cylinders through which air could freely circulate; with one of these, B, 300 grams of fresh manure (fowl's dung) was mixed. The mould contained 250 milligrams of N_2O_5 per kilo., and an appreciable quantity of nitrous acid, but no trace of ammonia. It was, therefore, in the last stage of nitrification when ammonia had disappeared, but small quantities of nitrites still remained. The sample A (not manured) showed a gradual increase in the quantity of nitric acid up to 282 milligrams of nitric anhydride per kilo., when the whole of the nitrous acid had disappeared. In the manured sample, B, the nitric acid decreased in two days to 230 milligrams of nitric anhydride per kilo., in four days to 190 milligrams, and so on. In the initial period, nitrous acid was formed, but subsequently disappeared; after 15 days, no trace of either nitric or nitrous acid remained; the quantity of ammonia, on the other hand, increased regularly and attained a maximum on the 29th day, after which it remained constant for five or six days. On the 35th day, nitrification recommenced, nitrous acid reappearing and the ammonia beginning to decrease; the transformation of the ammonia into nitrous acid and of the latter into nitric acid continued during three months, after which no trace of either ammonia or nitrous acid could be found, only nitric acid remaining in the soil.

The manuring of soils, therefore, gives rise to a cycle of phenomena, nitrification being first arrested and the nitrates and nitrites reduced until a maximum formation of ammonia is attained, when nitrification again commences. The destruction of the nitrates and nitrites in the soil is complete or partial, according as the supply of manure is abundant or otherwise. S. B. A. A.

Reducing Power of Micro-organisms. By T. LEONE (*Gazzetta*, **20**, 152—154).—The author criticises the methods and results of De Blasi and Travali (Abstr., 1890, p. 1453), and maintains that nitrification is a biological phenomenon taking place under the conditions described (see preceding abstract and 1890, 1453). The reduction of nitrates in the presence of rapidly developing germs takes place simultaneously with the oxidation of the organic compounds present, and is due to the abstraction of oxygen from the nitrates for that purpose. S. B. A. A.

Biogenesis of Hydrogen Sulphide. By DEBRAYE and LEGRAIN (*Compt. rend. Soc. Biol.* [9], **11**, 466—468).—It is well known that certain bacteria produce hydrogen sulphide from albuminous materials. The number of microbes that act thus is by no means limited, and by appropriate means nearly all of them can be made to produce the gas in cultures in which the action is anaërobic. The formation of the gas appears to depend on the amount of the nascent hydrogen present.

W. D. H.

Chlorophyllic Assimilation by Trees with Red Leaves. By H. JUMELLE (*Compt. rend.*, **111**, 380—382).—The relative activity of green and other leaves was compared by exposing them to sunlight under comparable conditions in a closed atmosphere containing a known quantity of carbonic anhydride, and determining how much carbonic anhydride was decomposed; the weights of the dried leaves being ascertained at the end of the experiment. The results show that in trees with red or coppery leaves, the chlorophyllian assimilation is always lower than in the same trees with green leaves, a result which explains the well known fact that trees of the former class increase in size much more slowly than those of the latter. In some cases the differences are very great; the assimilation of the green beech is about six times as great as that of the copper beech, and there is the same difference between the ordinary and the purple sycamore. C. H. B.

Sugars in Mushrooms. By E. BOURQUELOT (*Compt. rend.*, **111**, 534—536 and 578—580).—*Lactarius piperatus* Scop., when examined immediately after it is gathered, contains a considerable quantity of trehalose, but very little mannitol. If, however, it is dried and then treated with water, no trehalose is obtained; mannitol alone is present. The same phenomenon is observed if the mushrooms are merely kept for a few hours after being gathered, and hence the disappearance of the trehalose is a result of the continuance of the vital processes of the mushroom. This conclusion is confirmed by the fact that if the mushrooms are kept in a vessel filled with chloroform vapour, the trehalose remains, although the mushrooms become dark-brown and exude a large quantity of liquid.

Examination of various species of mushrooms at different stages of growth shows that when young they contain trehalose and no mannitol, in the middle period they contain both, and when mature they contain mannitol only. *Amanita mappa* is an exception, since in all stages it contains mannitol and no trehalose.

The conversion of trehalose into mannitol is a process of reduction, and is probably connected with the formation and maturation of the spores. In many species the phenomena are complicated by an increase in the amount of glucose that they contain, and in others by the appearance of glucose which is not present in the earlier stages of their growth. C. H. B.

Loss of Sugar in Beetroot. By G. MAREK (*Bied. Centr.*, **19**, 619—622; from *Deut. Landw. Presse*, **17**, 310—311).—The loss of sugar in beetroot is closely connected with the amount originally contained. Roots were examined in December, 1888, and in March 1889, the sugar being determined by the polarisation of the juice and by extraction with alcohol. The loss in all cases was very considerable. The loss is greatest with roots containing most sugar; the kind, soil, and manuring have less to do with it, and everything which raises the amount of sugar in the roots increases the liability to lose sugar. It is also shown that the higher the temperature at which the roots are kept, the greater is the amount of sugar which is lost. When roots which originally contain equal amounts of sugar lose unequally, the greatest loss will be in those which contain the greatest amount of non-saccharine substances. This fact is of importance in the selection of roots for seed. Comparative experiments were made with nitrogenous and phosphatic manures, the results of which show that phosphoric acid has no unfavourable effect on the durability of the roots, as is frequently stated.

In the manufacture of sugar, those roots which contain most sugar should be used first. N. H. J. M.

Behaviour of Tannin in Plants. By M. Büsgen (*Forsch. Gebiete agrik. physik.*, **13**, 305; from *Jena. Zeit. Naturwiss.*, **24**).—Experiments were made to determine whether a disappearance of tannin in any parts of plants can be shown to take place. Microchemical methods were employed. Kraus makes a distinction between "primary" tannin, which is produced with, and "secondary" tannin, which is formed without, the intervention of light. In certain cases both were found to disappear. Tannin was found to disappear from cells which were on the point of dying as well as from cells possessing more vitality. The author doubts whether the tannin is again used in building up. Direct proof of the production of tannin from sugar was obtained in a manner similar to that of the formation of starch from sugar. Portions of shade-leaves of various plants were placed with the upper side on a 10 per cent. solution of grape-sugar, the chief veins having been cut to facilitate the entry of the solution. Portions of the same leaves were similarly placed on water as a control experiment—a necessary precaution, as in many leaves the amount of tannin increases after they are cut off and kept in the dark. After four to six days, the leaves showed a considerable increase in the amount of tannin. It has still to be shown what intermediate compounds are formed, and also whether other substances besides grape-sugar will produce tannin. N. H. J. M.

Cultivation of Wheat in a Sterile Siliceous Sand. By Pagnoul (*Compt. rend.*, **111**, 507—509).—Calcium sulphate and natural phosphates were mixed with the sand; soluble salts were added by watering the experimental pots with solutions of definite strengths. Phosphates are indispensable; a yield of 46 quintals per hectare with a complete manure fell to 12 quintals in absence of soluble phosphate, and to 2 quintals when no phosphate was added at all. The ratio of grain to straw also depends on the supply of phosphate, and the suppression of phosphoric acid retards the maturing of the wheat by 10 days. Presence or absence of nitrogen is not of such vital importance, probably because the wheat can obtain a certain quantity from the air. Absence of nitrogen reduced the yield from 46 to 11 quintals per hectare. In a complete manure, nitric nitrogen has only a slightly greater efficiency than ammoniacal nitrogen, but in absence of potassium, the yield with the former is double the yield with the latter. It follows that the presence of potassium is essential when ammoniacal manures are used.

The proportion of nitrogenous compounds in the grain increases with the quantity of nitrogen placed at the disposal of the plant. It fell to 8—9 per cent. with a non-nitrogenous manure, but rose to 20 per cent., which is higher than the ordinary maximum, when the quantity of nitrogen supplied was greater than that existing in the most fertile soils.

Nitric nitrogen was never found in appreciable quantity in plants stinted of nitrogen, but rises to 0·2 per cent., especially in February and March, in those plants which had received nitrogen either in the form of ammonia or nitrates. In absence of potassium, the quantity of nitric nitrogen is very small, and traces of ammoniacal nitrogen are present.

C. H. B.

Examination of Potato-Spirit Liquor. By M. Kühn (*Bied. Centr.*, **19**, 628; from *Milchzeit.*, **18**, 926).—The following numbers show the percentages in the sample of the liquor which was used as cattle food:—

Fat.	Proteïn.	Pure ash.	Crude fibre.	Non-nitrogenous extractives.	Sand in pure ash.
0·13	1·61	1·20	0·43	3·50	0·44

N. H. J. M.

The Behaviour of Sandy Soil towards Superphosphate. By A. Thomson (*Bied. Centr.*, **19**, 585—588).—The absorptive power of pure sea-sand for phosphoric acid was determined as well as that of the same sand containing known amounts of orthoclase, of calcium carbonate, of ferric and aluminum hydroxides, of calcium carbonate and orthoclase, and of calcium carbonate and the mixed ferric and aluminium hydroxides. The effect of sodium chloride and potassium nitrate on the process of absorption was also studied.

Pure sand offers no resistance to the extraction of the phosphoric acid of superphosphate by pure water, or solutions of sodium chloride and potassium nitrate. The addition of orthoclase is without effect. Calcium carbonate combines quickly with the soluble phosphoric acid; and the hydroxides of iron and aluminium are very active in retaining phosphoric acid, especially when used in conjunction with calcium carbonate. 1 or 2 per cent. solutions of sodium chloride extract from superphosphate rather less phosphoric acid than distilled water; but in presence of calcium carbonate and ferric and aluminium hydroxides, the dilute salt solution extracts more phosphoric acid than water alone. Dilute potassium nitrate solutions diminish the absorptive power of all the substances employed more than sodium chloride.

The results point to the conclusion that the full benefit of manuring with superphosphate (in a sandy soil) will only be attained when large amounts of lime or smaller amounts of lime and ferric and aluminium hydroxides are well distributed in the soil, and when the soil does not contain too much nitrate. In absence of these conditions, the application of superphosphate should be avoided. The methods of experimenting and the apparatus employed are described in detail in the original paper (*Inaug. Diss. Dorpat*, 1890).

N. H. J. M.

Composition of Bone-meal. By J. Stocklasa (*Chem. Zeit.*, **14**, 1—2, 21, 32—33).—The author has examined bone-meal obtained by different methods. In the first series of experiments, bones were digested for six hours in soft water, at 95°, by which they yielded 2·3 per cent. of fat, and lost 0·53 per cent. of nitrogen; they were then steamed, either under a pressure of 2·5 atmospheres for 75 minutes (Results A), or under 1·5 atmospheres for 60 minutes (Results B), or under 0·5 atmosphere for an hour (Results C), dried at 40°, pulverised, and the meal and grit analysed, with the results given in the table. In the second series of experiments, it was sought to extract the fat by means of light petroleum:—Results D were obtained from meal prepared from bone containing 9·2 per cent. of fat; the extraction was conducted under 1·2 atmospheres, the residual petroleum expelled with steam, the extracted bones dried at 45°, and pulverised. For Results E, the bones containing 8·8 per cent. of fat were extracted without pressure, and treated like D, but dried at 36°. Results F: Bones containing 8·7 per cent. of fat, extracted under 1·3 atmospheres, then steamed under 2 atmospheres pressure for 20 minutes, &c. Results G: Bones containing 8·9 per cent. of fat, extracted under 1·2 atmospheres pressure, then steamed under 3 atmospheres for 30 minutes, &c.

Results.	A.	B.	C.	D.	E.	F.	G.
Organic non-fatty matter	26·38	27·82	29·54	33·67	31·24	34·25	26·34
Fat	5·51	9·38	11·32	7·84	6·42	9·06	2·85
Inorganic matter............	56·24	52·43	50·43	49·35	48·93	47·87	61·69
Water	11·87	10·37	8·71	9·14	8·41	8·82	9·12
Nitrogen	3·77	4·05	4·25	4·83	4·36	4·96	3·94

Steaming, when the pressure is sufficiently great to remove fat, also removes much nitrogen. By the second method of extraction, less nitrogen is lost, the coarse crushed bone makes a superior granular charcoal, and the gelatin from the bone grit is excellent, whilst the fat contains less calcium and ammonium oleates, palmitates, and stearates. For agricultural purposes, the fat impedes decomposition, both of the nitrogenous matter and the phosphate. The fragments of bone containing most fat are more brittle; hence the meal is found to contain more fat than the grit, and so on up the scale of coarseness. The author gives results showing this. He regards finely pulverised bone meal deprived of fat as an excellent manure, superior to basic slag, and not even second to precipitated phosphate in action, its apparent failure, hitherto being attributed to want of attention to the points now set forth in the present paper.

D. A. L.

Amount of Fat in Bone-meal. By J. MERZ (*Chem. Zeit.*, **14**, 95).—Referring to Stocklasa's communication (preceding abstract), it is considered that justice is not done to the extraction method in the results quoted; therefore the author of the present note calls attention to three experiments of his own, wherein the fat in bones was reduced to 0·32, 0·28, and 0·26 respectively, in from six to seven and a half hours, by extraction with petroleum without pressure, the latter not being regarded as a factor in the extraction of fat on a large scale any more than it is on a small scale in laboratory fat estimation. In fact the more the former operation is made to resemble the latter, the greater is the yield of fat, and the better the quality of the bone-meal.

D. A. L.

Analytical Chemistry.

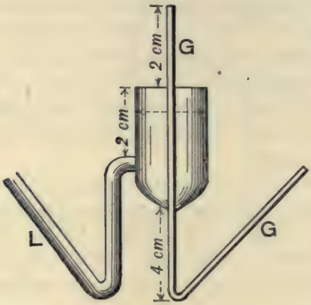
Estimation of Hydrogen Chloride in Solutions of Hydroxylamine Hydrochloride. By J. A. Muller (*Bull. Soc. Chim.* [3], **3**, 605).—Phenolphthaleïn is unaffected by solutions of hydroxylamine hydrochloride, and the amount of acid present may be estimated by means of a standard solution of sodium hydroxide, free from carbonate, using phenolphthaleïn as the indicator. Pyridine, picolines, and lutidines behave similarly. T. G. N.

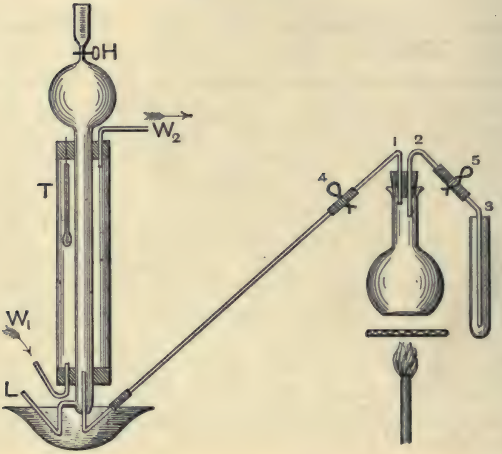
Estimation of Sulphur in Inorganic Sulphides. By L. Blum (*Zeit. anal. Chem.*, **29**, 411—412).—The method published by Jannasch (Abstr., 1889, 1244, and 1890, 1187) is not new, having been already brought forward by Sauer, in 1873 (Abstr., 1873, 939). M. J. S.

Estimation of Nitrogen by the Schultze-Tiemmann (Schloesing's) Method. By F. Cochius and T. Moeller (*Chem. Zeit.*, **14**, 33).—Low results are obtained by this method, especially in the examination of explosives. This is attributed by the authors to the addition of too much water, and to the want of proper relationship between the size of the apparatus used and the quantity of material employed. In some test experiments they used a long-necked 350 c.c. flask, a measuring tube of 150 c.c. capacity, ferrous chloride solution containing 70 grams in 100 grams of water, hydrochloric acid of about 37 per cent., and employed 0·3—0·4 gram of potassium nitrate, 5—15 c.c. of the ferrous chloride solution, and twice the quantity of the hydrochloric acid. The ordinary course of operation was followed, avoiding unnecessary boiling to drive out the air. When 25 to 50 c.c. of water was added, the analysis lasted 30 to 40 minutes, and the results varied between 13·76 and 13·86, mean 13·81, whilst with 80 to 150 c.c. of water the variation in the results was from 13·05 to 13·39, mean 13·21, and the analysis lasted 70 to 90 minutes. D. A. L.

Estimation of Nitrogen in Sodium Nitrate. By O. Foerster (*Chem. Zeit.*, **14**, 509—510; compare Abstr., 1889, 547, 746).—Two or three grams of the nitrate is dried at 150° or by heating to incipient fusion, weighed, and repeatedly evaporated to dryness on a water-bath in a tared crucible, with 25 c.c. of about 19 per cent. hydrochloric acid. After about the third evaporation, the nitrate is completely converted into chloride, which is dried at 150°, ignited slightly, and weighed, and the nitrogen calculated from the difference. The method yields satisfactory results, but only in the absence of other substances, which would be attacked by hydrochloric acid. D. A. L.

Estimation of Nitric Nitrogen as Nitric Oxide. By F. Scheiding (*Chem Zeit.*, **14**, 635—637).—For estimating nitric nitrogen as nitric oxide, the author has devised and employs the apparatus shown in the drawing, which is provided with a measuring tube having a globular expansion, a glass tap H with a small funnel at the top, and a special arrangement intimately attached by india-rubber tubing or fusion to the bottom. In operation, tube L is connected in a suitable manner with a movable reservoir containing sodium hydroxide, sp. gr. 1·25, with which the apparatus is charged to the level of 4 by raising the reservoir, and clip 4 is closed. The substance is placed, along with a little water, in a 200—250 c.c. flask, to which the stopper and tubes are fitted, connections made, and to expel the air through tubes 2 and 3, the water in the flask is boiled until the water into which tube 3 dips is caused to boil by the issuing steam, clip 5 is then closed, and the air still in tube 1 driven into the measuring tube by opening clip 4, which is again closed, and the flame removed from below the flask. The measuring tube is filled to the top with sodium hydroxide, and tap H is closed. 20—25 c.c. of cold saturated ferrous chloride, and then 8—10 c.c. of concentrated hydrochloric acid are carefully drawn into the flask through tubes 2 and 3, which are then washed with water in the same way; the flask, suspended a few cm. above the wire gauze, is now heated, and as





soon as a pressure is indicated in the india-rubber tube at 4, that clip is opened, the nitric oxide passes into the measuring tube, and by the time the liquid has volatilised in the flask, all the nitric oxide is concluded to be in the measuring tube. The temperature in the jacket tube surrounding the measuring tube is made to correspond with that in the vicinity of the bulb, and the level in the reservoir being adjusted to that in the measuring tube, the volume is read off, and after the necessary corrections are made, the percentage of nitrogen is calculated therefrom. The saucer under the measuring apparatus is filled with water to keep the tubes immersed in it cool. For substances which might be decomposed by boiling with water, a tap funnel is fitted to the flask, and is used for charging it. D. A. L.

Estimation of Nitrogen in Organic Substances by means of Alkaline Permanganate. By R. L. Wagner (*Chem. Zeit.*, **14**, 269).—The author some years ago recognised the possibility of oxidising nitrogenous organic substances by means of alkaline permanganate, without the formation of ammonia. In his experiments he mixed 0·5 to 1 gram of substance with 25—30 times its weight of potassium permanganate, and 5 c.c. of 25 per cent. potassium hydroxide, placed the mixture in a tube closed at one end, terminating at the other in a capillary for the escape of oxygen, warmed in a water-bath to aid admixture, and then heated at 150—170° in an air-bath for two to two and a half hours. The contents of the tube were turned into a porcelain basin, the excess of manganate reduced with manganese sulphate and sodium carbonate, and the nitric acid determined in the clear liquid by a modification of Eder's method; but irregularity of combustion and breaking of tubes rendered the method practically useless, except, perhaps, for substances soluble in alkalis. Non-volatile nitro-derivatives and ethereal nitrates can be safely oxidised by alkaline permanganate in a porcelain dish, excess of permanganate being subsequently reduced with alcohol, and the diluted filtrate treated with ferrous sulphate, zinc-dust, and hydrochloric acid; the nitrogen is then estimated as ammonia, by any of the usual distillation methods.

Carbon bisulphide and thiophen can be oxidised by similar treatment, and the sulphur estimated in them; they are enclosed in thin glass bulbs, and placed in tubes containing the alkaline permanganate; the tube is sealed up, the bulb broken, and the digestion proceeded with. **D. A. L.**

Detection of Foreign Raw Phosphates in Powdered Basic Slag. By L. Blum (*Zeit. anal. Chem.*, **29**, 408—411).—The relative superiority of basic slag as a fertiliser over natural phosphatic minerals, owing to its ready absorbability, and the high price which it has in consequence attained, have led to its falsification with other raw phosphates. Only such are likely to be used as, from their low percentage of phosphoric acid, cannot profitably be worked up as superphosphate, and these in most cases contain much calcium carbonate. Fresh basic slag is almost absolutely free from carbonates, and even on long exposure to air, absorbs very little carbonic acid

(2·47 per cent. was found in an extreme case), so that the presence of much carbonate in a specimen would be enough to throw suspicion on it. A low percentage of iron and manganese might furnish an additional indication, since these metals are rarely present in natural phosphates. In estimating the carbonic acid by decomposition with an acid, some chromic acid should be added, to prevent evolution of hydrogen sulphide from the sulphides present, but a simple estimation of the loss on ignition would generally allow an opinion to be formed. M. J. S.

Estimation of Water in Superphosphates. By J. Stoklasa (*Zeit. anal. Chem.*, **29**, 390—397).—Pure monocalcium tetrahydrogen phosphate, $CaH_4(PO_4)_2 + H_2O$, loses its water of crystallisation at 100°, but only completely after 40 hours. It may be kept at 105° for 20 hours with but little change, but on longer heating at the same temperature begins to show decomposition. At higher temperatures, the amount of change is dependent not alone on the temperature, but also on the time of drying. The statement of Drewsen (Abstr., 1881, 465) that drying even at 300° does not diminish the proportion of soluble phosphate, but merely reduces it to a soluble pyrophosphate, cannot be confirmed for pure or nearly pure monocalcium phosphate. It might be true for a superphosphate in which free phosphoric acid constituted 80 per cent. of the total soluble phosphoric acid.

On drying for one hour at 200°, one-half of the monocalcium phosphate undergoes decomposition, thus:—$4CaH_4(PO_4)_2 = Ca_2P_2O_7 + Ca(PO_3)_2 + CaH_2P_2O_7 + 2H_3PO_4 + 4H_2O$. At lower temperatures for the same length of time, the proportion decomposed is smaller, but if the time is prolonged, a further decomposition takes place even at 150°, and less free phosphoric acid is found in the soluble part. A temperature of 200° sufficiently prolonged results in the following decomposition:—$4CaH_4(PO_4)_2 = 3Ca(PO_3)_2 + CaH_2P_2O_7 + 7H_2O$, whilst at 210°, there remains nothing but insoluble, glassy calcium metaphosphate. In presence of free phosphoric acid, the contrary action may on heating take place, thus: $Ca_2P_2O_7 + 2H_3PO_4 = 2CaH_2P_2O_7 + H_2O$, and thus the soluble phosphoric acid actually undergo increase. M. J. S.

Separation of Barium from Strontium. By R. Fresenius (*Zeit. anal. Chem.*, **29**, 413—430; see Abstr., 1890, 924).—All attempts to obtain complete separation by means of chromic acid in a single precipitation resulted in failures. The seemingly satisfactory separation obtained by Frerichs and by Russmann (next abstract) resulted from the accidental compensation of opposite errors, since they washed the barium chromate with acetic acid, in which it is distinctly soluble, and weighed it after drying at 110°, at which temperature it still retains some moisture. In a solution containing alkaline acetate and dichromate, barium chromate is, however, quite insoluble. It can also be rendered anhydrous without decomposition by ignition at a dull red heat, even the portion adhering to the filter reoxidising after temporary reduction. By double precipitation of the barium, a complete separation can be effected even when the proportion of strontium is large. The solution of the chlorides is feebly acidified with acetic acid, and diluted until it contains not more than 0·5 per cent. of the bases, then precipitated hot with an excess of ammonium chromate, which has been carefully neutralised with ammonia. After cooling for an hour, the precipitate is washed by decantation with very dilute ammonium chromate until the washings no longer give a precipitate with ammonium carbonate, and then further with warm water until the washings are scarcely coloured by silver nitrate. The precipitate is then dissolved in the smallest possible quantity of nitric acid, and the solution again diluted and heated. Ammonium acetate is added in sufficient quantity to displace the free nitric acid by acetic acid, and then ammonium chromate until the odour of acetic acid has completely disappeared. After an hour, the liquid is poured through a filter, the precipitate is digested with hot water, cooled, filtered, and washed thoroughly with cold water. It is then free from strontium, whilst the filtrates contain no barium. Double precipitation from neutral or alkaline solutions has not been successful.

M. J. S.

Separation of Barium, Strontium, and Calcium. By A. Russmann (*Zeit. anal. Chem.*, **29**, 447—454; from *Inaug. Diss. Berlin*, 1887).—Barium cannot be satisfactorily estimated by Frerichs' method (precipitation from an acetic acid solution by normal potassium chromate), since the filtrate always contains traces of barium, and some potassium chromate is carried down by the precipitate. The precipitate will also contain strontium, if the proportion of the strontium in the solution exceeds 30 parts per 100 of barium. Calcium is not so precipitated. The simplest way to ascertain the weight of the barium chromate, is to dissolve it in dilute hydrochloric acid, add potassium iodide, and immediately titrate with thiosulphate. Diehl's method for separating barium and calcium by digesting the sulphates with sodium thiosulphate solution is complicated by so many sources of error that it cannot be recommended. Fresenius' method of separating barium and calcium by dilute sulphuric acid in a solution acidified with hydrochloric acid is thoroughly satisfactory. The method of Sidersky (Abstr., 1883, 509) for separating strontium and calcium only yields approximate results. For separating barium and calcium, it is, however, serviceable. Bloxam's method (Abstr., 1886, 920) is not suitable for quantitative separations, as the strontium sulphate carries down with it considerable quantities of calcium, and the calcium ammonium arsenate cannot readily be brought into a form for weighing in which it contains a constant proportion of calcium. Fleischer's method for separating barium and calcium by digestion with 3 parts of potassium sulphate and 1 part of carbonate, followed by titration of the calcium carbonate in the weighed precipitate gives good results. Lastly, Leison's method for the estimation of the individual alkaline earths, by precipitation with oxalic acid and alcohol, and titration of the oxalic acid in the precipitate by permanganate, is accurate. The barium oxalate must be dissolved by hydrochloric acid, as it is not completely decomposed by sulphuric acid. Strontium and calcium oxalates can be decomposed by sulphuric acid. The solutions must not be filtered through paper, and must be highly dilute. Ignition of the oxalates is, however, as a rule, the quicker process. M. J. S.

Estimation of Cadmium in the Products of Zinc Manufacture and in Calamine. By W. Minor (*Chem. Zeit.*, **14**, 4, 34, and 348—349).—The material is dissolved in hydrochloric acid, treated with hydrogen sulphide, and the precipitate washed with hot water, dissolved in hydrochloric acid, heated to boiling, and poured into dilute sodium hydroxide likewise heated to boiling. This precipitate, after washing with hot water, is ignited in a current of oxygen, and weighed as cadmium oxide. Material containing but little iron, such as "pure cadmium," is dissolved in hydrochloric acid, and precipitated directly with the sodium hydroxide. This method of precipitation may also be used to separate zinc and cadmium in the ordinary method of examining calamine; the ammoniacal solution containing the zinc and cadmium is rendered slightly acid and poured hot into the hot hydroxide, &c.

In the method described in the last of the three papers, the material is dissolved in hydrochloric acid, filtered from undissolved lead, precipitated with hydrogen sulphide, the precipitate, containing zinc and an inconsiderable amount of arsenic, is washed, dried, weighed, dissolved in dilute hydrochloric acid, and treated with sodium hydroxide in excess. The cadmium hydroxide is filtered off, and the zinc titrated in the filtrate with sodium sulphide, calculated to zinc sulphide, and deducted from the weight of the cadmium sulphide precipitate. In another method (requiring the absence of other metals precipitated by sodium hydroxide) after removal of iron with ammonia, the solution of zinc and cadmium is nearly neutralised with hydrochloric acid, and then treated with sodium hydroxide. The precipitate of cadmium hydroxide is dissolved in dilute hydrochloric acid, evaporated to dryness, dissolved in water, and titrated with standard sodium hydroxide, using litmus or sodium sulphide papers as indicators. Good results have been obtained by both methods, the first being the more suitable in the presence of much zinc and *vice versâ*. D. A. L.

Estimation of Cadmium as Sulphide by Precipitation with Sodium Sulphide Solution. By W. Minor (*Chem. Zeit.*, **14**, 439—440).—The material is dissolved in hydrochloric or nitric acid, and the lead separated by sulphuric acid; the solution is then treated with soda, and the precipitate digested with ammonia. The ammoniacal solution is free from lead, zinc, and iron, but contains all the cadmium, which can then be determined by means of sodium sulphide solution, either volumetrically by titration, using ferric hydroxide as indicator, or gravimetrically by precipitating, and weighing the precipitate after drying for some hours at 140—145°. D. A. L.

Volumetric Estimation of Zinc and Copper. By E. Donath and G. Hattensaur (*Chem. Zeit.*, **14**, 323—325).—Various experiments have been made by the authors. They find that for titrating zinc by Schaffner's method, it is better to use sodium hydrosulphide (prepared by adding a known volume of dilute sodium hydroxide to an equal volume of the same solution previously saturated with hydrogen sulphide) than a solution of the crystalline sulphide of commerce; however, in using this reagent in solutions containing tartaric acid and ammonia, the iron commences to precipitate before all the zinc is converted into sulphide. The estimation of zinc by using excess of ferrocyanide, after the removal of the iron, and titrating back with permanganate does not answer, since in the cold a clear solution cannot be obtained, whilst if warm, decompositions occur which cause irregularities. It is noticed that ferrocyanide precipitates zinc but not iron in the presence of tartaric acid and ammonia, and that the excess of either of these substances does not seriously disturb the relative quantity of 1 mol. ferrocyanide to 2 atoms of zinc; therefore 1 c.c. of a solution containing 33·5 grams of potassium ferrocyanide per litre corresponds with 0·010 gram of zinc. As small an excess of ammonia as possible, and a hot solution, are favourable to the precipitation. The zinc precipitate is not decomposed by acetic acid; therefore, by placing drops of this acid and the solution under examination in contact, in the presence of iron, a coloration indicates complete precipitation of the zinc. The following method is based on these considerations:—3 to 4 grams of material is dissolved in hydrochloric acid with some nitric acid, diluted to a definite volume with water, an aliquot part filtered, treated with 20—25 c.c. of concentrated tartaric acid solution, a slight excess of ammonia added, and the liquid warmed to about 80°. The ferrocyanide is now run in until the precipitation of the zinc is complete, as indicated in the manner described above. The proportion of iron to zinc in the solution under examination should be the same as that present in the solution used for standardising the ferrocyanide.

Under similar circumstances, copper is precipitated in a like manner, but the precipitation is greatly influenced by ammonia; therefore the solution for titration should be neutral or nearly so. The ferrocyanide is standardised from a solution of copper of known strength, and cannot be approximated to by the weight of ferrocyanide employed, inasmuch as the composition of the copper precipitate is uncertain. Copper and zinc may be estimated in the same solution by this method; first both are titrated, then the copper is precipitated out of another portion of solution, and the zinc alone titrated, &c.

D. A. L.

Estimation of Lead by Phosphomolybdic Acid. By H. Beuf (*Bull. Soc. Chim.* [3], **3**, 852—855).—To the boiling neutral solution of the metal, an aqueous solution of phosphomolybdic acid is added until the supernatant liquid is coloured yellow by the excess of reagent used. After washing, the precipitate is dried at 90—100° and weighed. It forms a dense, white powder which is insoluble in water (1 in 500,000) and aqueous ammonia, but dissolves in nitric and in acetic acids; it contains 54·8 per cent. of lead, and corresponds with the formula $Mo_{25}Pb_{25}P_2H_{14}O_{112}$; at a high temperature it loses 7 mols. H_2O.

By decomposition of the precipitate with dilute sulphuric acid and zinc at a gentle heat, a brown liquid is obtained, which may be titrated for lead by a solution of permanganate which has been previously standardised against a solution resulting from the similar treatment of a known weight of a lead salt.

The phosphomolybdic acid is made by evaporating to dryness a solution of ammonium phosphomolybdate in nitric acid. Iron is eliminated by a previous treatment with sodium hydroxide, copper, potassium, and ammonium by washing the mixed phosphomolybdates with ammonia-water, but the presence of zinc or arsenic vitiates the estimation. T. G. N.

Separation of Copper from Arsenic by the Electric Current. By L. W. McCay (*Chem. Zeit.*, **14**, 509).—Under the influence of the current from four to six Meidinger elements, alkaline arsenates remain in solution, whereas copper is completely and quantitatively precipitated, and has been estimated with good results. Moreover, the copper is quite free from arsenic, and the solution may be safely employed for the determination of the original amount of the latter metal. D. A. L.

Estimation of Aluminium in Commercial Aluminium. By G. Klemp (*Zeit. anal. Chem.*, **29**, 388—390).—The process employed for zinc (Abstr., 1890, 1190) cannot be applied to aluminium since, even with highly dilute alkali and a large excess of iodate, hydrogen is always evolved, but by dissolving the aluminium in potash, and burning the hydrogen in Fresenius' apparatus, a very accurate estimation can be made. About 1 gram of the metal in filings is placed in a 150 c.c. flask with a little vaselin to prevent frothing, and the potash solution (35 grams of KOH in 100 c.c.) is added gradually, with warming towards the close. The operation takes about 45 minutes. M. J. S.

Estimation of Alumina in Bread, &c.; Solubility of Aluminium Phosphate in Acetic Acid. By W. C. Young (*Analyst*, **15**, 61—63; 83—84).—In Dupré's process, the aluminium is precipitated as phosphate from an acid solution containing ammonium chloride and acetate, and is collected after remaining all night in the cold. Test analyses, with weighed quantities of alum, show that under these conditions the results are much below the truth. The best result (from a mixture of alum, sodium phosphate, and acetic acid) was obtained by boiling the mixture both before and after the addition of ammonium acetate, and filtering immediately. The amount of ammonium acetate must not be too small, nor that of acetic acid too large. For 0·1 gram of potash alum, there was used 1 gram of ammonium acetate and 5 c.c. of ordinary acetic acid. The presence of ammonium chloride has little effect when the liquid is filtered immediately after boiling, but lowers the result if the precipitation is performed in the cold, or the mixture is allowed to cool before filtering. M. J. S.

Estimation of Iron Oxide and Alumina in Phosphates. By R. Jones (*Chem. Zeit.*, **14**, 269—271).—The author criticises the methods employed until recently, and recommends as the best the following combination of Glaser's method, slightly modified, with part of Stutzer's method. The phosphate is dissolved in hydrochloric and nitric acids, made up to a definite volume, an aliquot part taken and treated with a quarter of its volume of sulphuric acid of sp. gr. 1·84, and its own volume of 95 per cent. alcohol, making up to definite volume with the alcohol; after 12 hours, the gypsum is collected, and when weighed, gives good results for calcium in absence of much magnesium. The alcohol is driven off from the filtrate, which is rendered alkaline with ammonia and boiled to completely drive off the ammonia. The precipitate may be weighed, and half the weight taken as iron oxide and alumina, which gives good results, or it may be treated with molybdic solution, the phosphoric acid separated in the usual way, the iron and alumina precipitated wlth dilute ammonia, redissolved in hydrochloric acid, reprecipitated, &c., and weighed. D. A. L.

Titration of Chromates, Barium Salts, and Sulphates. By P. SOLTSIEN (*Chem. Centr.*, 1890, ii, 217—218; from *Pharm. Zeit.*, **35**, 372).—The titration of solutions of barium salts with potassium dichromate, and inversely the titration of chromates with barium salts, may be readily performed with either hæmatoxylin or logwood extract as indicator. A solution of barium chloride is prepared equal to one of potassium dichromate, and for the determination of barium salts, potassium dichromate is run in from the burette until a drop placed on a warmed porcelain plate with a drop of hæmatoxylin just shows the formation of a blue-black coloration. The solution to be titrated must be neutral, and may not contain more than the merest trace of either acetic acid or ammonia. Chlorides and nitrates do not interfere with the reaction, nor does rosolic acid, which latter may be used as an indicator for the titration of solutions of salts of barium. If the solution of a chromate contains sulphates, the titration with barium chloride gives the total quantity of the two salts, from which must be deducted the amount of the latter as determined gravimetrically.

For the determination of the combined sulphuric acid, an excess of barium chloride solution is added, and the excess determined by titration with potassium dichromate.

Salts of aluminium, copper, and iron must be removed from the solutions. J. W. L.

Estimation of Antimony by Marsh's Method. By A. VAN BYLERT (*Ber.*, **23**, 2968—2971; compare Kühn and Saeger, Abstr., 1890, 1187).—For the estimation of antimony in alloys of tin, silver, and antimony, the author recommends the following process:—A three-necked Woulffe's bottle is connected on the one hand with an apparatus for evolving carbonic anhydride, and on the other with the usual calcium chloride tube and hard glass tube. The central neck of the Woulffe's bottle is fitted with a wide tube reaching to the bottom of the flask. About 0·5 gram of the alloy is dissolved in 20 c.c. of mercury at 60°, and poured, after cooling, into the flask. 100 c.c. of 10 per cent. sulphuric acid is then added through one of the side tubes, and the air expelled from the apparatus by carbonic anhydride. A freshly prepared sodium amalgam, obtained by dissolving 5·5 grams of sodium in 25 c.c. of mercury, is then added drop by drop through the wide tube. The sublimate of antimony quickly appears in the heated tube; the apparatus is then periodically shaken, care being taken that no liquid is allowed to pass into the central tube. After the evolution of gas has ceased, carbonic anhydride is again passed through the apparatus to expel all the hydrogen and hydrogen antimonide. The mercury solution is then poured off, dried with filter-paper, and divided into two equal portions, one of which is returned to the cleaned and dried apparatus, and covered with 75 c.c. of a 10 per cent. sulphuric acid, whilst the other is mixed with 3 grams of sodium, and added drop by drop through the central tube as before.

The results obtained are fairly accurate, but might possibly be improved by employing hydrogen in place of carbonic anhydride for driving out the air. Another source of error is the oxidation which takes place in the manufacture of the alloy, and during its solution in the mercury. H. G. C.

Estimation of Hardness of Natural Waters. By E. L. Neugebauer (*Zeit. anal. Chem.*, **29**, 399—401).—The author proposes the following modifications of Clark's test. The standard water is a mixture of 8 vols. of calcium sulphate solution of 12° of hardness with 2 vols. of a 12° magnesium sulphate solution. Of this mixture, 100 c.c. is used. The soap solution is of such strength that 12 c.c. is required for the 100 c.c. of standard water. The following new table has been drawn up from titrations of the standard water diluted to the required degrees:—

Hardness............	0°	1°	2°	3°	4°	5°	6°
C.c of soap solution ..	0·6	1·7	2·8	3·9	4·9	5·9	6·9
Hardness............	7°	8°	9°	10°	11°	12°	
C.c of soap solution ..	7·8	8·7	9·6	10·4	11·2	12·0	

and a special burette (titanometer) constructed, the readings of which give at once the degrees of hardness. M. J. S.

The Analysis of Sulphurous Waters. By D. Vitali (*Chem. Centr.*, 1890, ii, 166; from *L'Orosi*, **13**, 73—78).—Thiosulphates may be detected by the addition of potassium nitrite and a mineral acid or acetic acid. Nitric oxide is liberated, and the solution is thereby coloured yellow; later, sulphur is precipitated, and the liquid becomes milky. This reaction is extremely delicate, 0·0001 per cent. of thiosulphate being detectable. In testing for nitrites in presence of thiosulphates with potassium iodide and starch, this reaction of the thiosulphate may prevent the formation of the blue iodide of starch, a yellow coloration being produced instead. In testing for iodine, in presence of thiosulphates, with potassium nitrite and an acid, it is better to evaporate the water to dryness after neutralising with sodium carbonate, and then to extract the residue with absolute alcohol, which dissolves the iodide, leaving the thiosulphate undissolved. In the case of waters containing large quantities of calcium sulphate, it is recommended to first precipitate the calcium as calcium carbonate before determining the silicic anhydride. In order to prevent the precipitation of sulphur during the evaporation of water for determination of the total solid residue, the author recommends that a current of hydrogen should be passed through the water.

J. W. L.

Examination of Water for Contamination by Gas Works. By F. DICKMANN (*Zeit. anal. Chem.*, **29**, 398—399).—In a specimen of water from a brook which had suffered contamination from a neighbouring gas works, and by which poultry had been poisoned, the author detected traces of a substance giving the reactions of diphenylamine. Owing to the stability of this compound and the sensitiveness of its reaction with nitric acid, its presence might be used as a proof of contamination by tar-water, if it should be found to be a constant constituent of that liquid. M. J. S.

Detection and Estimation of Organic and Inorganic Poisons in Corpses. By A. SEYDA (*Chem. Zeit.*, **14**, 31—32, 51—53, 128—129, 181—184, and 198—200).—The author describes his system of examining corpses. The chemical examination proper is preceded by a preliminary examination of the blood, urine, and contents of the stomach and accessories.

The *blood*, when not too decomposed to show the absorption bands, is examined spectroscopically; if dry, it is dissolved in water, and made very slightly alkaline with sodium hydroxide; the two oxyhæmoglobin bands and the intermediate hæmoglobin band merge into one continuous band in partially decomposed blood; the faint band in the red is attributable to methæmoglobin in alkaline material or to hæmatin in acid blood. In the former case, further examination is only made under exceptional circumstances, such as the presence of hydrogen sulphide not emanating from ordinary putrefactive processes; but, in the latter case, the red band being due to hæmatin, is regarded as indicating the presence of other reducing agents, or of acids, potassium chlorate, ferricyanides, nitroglycerol, or nitrobenzene, which are tested for in the urine and in parts of the body. Other isolated lines in the red are carefully noted, and carbonic oxide is sought for; the presence of hæmatin, already reduced or otherwise, indicates the absence of carbonic oxide poisoning; carbonic oxide hæmoglobin is recognised in presence of oxyhæmoglobin and hæmoglobin by the mere displacement of the absorption band towards the red part of the spectrum when ammonium sulphide is added; chemical tests with sodium hydroxide with or without calcium chloride are considered of little value.

In *the urine*:—Notes are taken of the quantity, colour, odour, of reactions as to the presence of blood, albumin, and sugar, of the action in alkaline copper solutions, of the behaviour towards barium chloride before and after treatment with hydrochloric acid, and of the occurrence of balsams, alkaloïds, soluble metallic poisons, and of such salts as potassium chlorate, iodide, or bromide.

The *contents of the stomach* are examined in the dark for phosphorescence, which is only due to phosphorus in acid mixtures, otherwise fungoïd growth may cause it. The odour of the contents of the stomach may be acid, alkaline, like decayed cheese, or they may have a specific odour, or be putrid; sometimes they are well preserved, and have a sweetish, repulsive odour, observed by the author in cases of arsenical poisoning. *Food magmas* and *vomits* are carefully sampled, treated with alcohol and then with ether, and examined macro- and micro-scopically. The alcoholic extract is examined for oxalates and foreign bases and acids; matters found in the folds are also examined. The arsenic test is applied, and an aqueous extract of the magma is examined for soluble poisons.

For the chemical examination proper, parts of organs, finely divided, are heated with water in a boiling water-bath for several hours, acidified with tartaric acid, and distilled with steam. Two fractions are made: the first will contain the more volatile matters, such as alcohol, aldehyde, acetone, chloroform, nitrobenzene, ethereal oils, turpentine, camphor, amines, and their volatile combinations; the other, the remains of these more volatile products, and any less volatile substances, such as fatty acids, phenol, hydrocyanic acid, &c. A plain distillation of alkaline material is required at times; if, however, the presence of chloral hydrate or hydrocyanic acid and ferrocyanides is suspected, the finely divided organs are first moistened with potash or with hydrogen sodium carbonate respectively. A steam distillation from alkaline solution, when necessary, is best effected, not directly, but with the liquid obtained by extraction with water and tartaric acid. The residue from the acid distillation is employed in testing for alkaloïds.

The odour, colour, opalescence, quantity, &c., of the first fraction of the acid distillate are noted. It is tested with silver nitrate, both in nitric acid and in ammoniacal solution, with sodium nitroprusside, potash, and acetic acid; with alkaline permanganate; with iodine and potash (iodoform reaction); with zinc-dust and hydrochloric acid for nitrobenzene; with hydrochloric acid and alcoholic phloroglucinol for ethereal oils (a reaction frequently takes place, but too much dependance is not to be placed on it; it is better to examine the *urine* for some of these substances, also for altered camphor). The reagents for turpentine oil, in tangible quantities, are a mixture of fresh guaiacum alcohol and fresh citronella oil. Resorcinol and potash are better reagents for detecting chloroform than the isonitrile test. A quantitative examination for these substances is seldom possible, with the exception of alcohol, but this cannot be estimated by distillation in the presence of amines; therefore it is oxidised to acetic acid as follows.

A portion of the distillate is redistilled, the first portions collected are dried with potassium carbonate, distilled again, treated with sodium dichromate and sulphuric acid, rendered alkaline with potash, boiled to eliminate amine bases, then acidified, steam distilled, and the distillate, containing the acetic acid, titrated; any sulphuric acid, if accidentally present, being estimated and allowed for. The author attaches great importance to the estimation of alcohol, especially in the case of children. Various parts of corpses of persons addicted to alcohol yield distillates containing alcohol, but not pure ethyl alcohol; therefore such distillates reduce alkaline permanganate, &c., give the iodoform reaction, and yield an inflammable distillate on redistillation from potassium carbonate. Alcohols readily evaporate from corpses, the more volatile disappearing first.

Passing on to the second fraction from the acid distillation, phenol, as a normal product of the decomposition of albuminoïds, is frequently detected by Millon's reagent, less readily by bromine-water. Large quantities of phenol are estimated by filtering the fraction containing it from the fatty acids, extracting with ether, drying the ethereal residue over sulphuric acid, and weighing, taking precautions against the phenol creeping over the edge of the evaporating dish. As regards hydrocyanic acid, the distillate is tested with copper sulphate and guaiacum, and if the reaction is noticed, it is confirmed by some other test, and the acid determined as silver cyanide. Phosphorus is generally recognised by the phosphorescence, but if this does not occur phosphorous acid must be tested for and estimated in the residue. In examining the distillate for phosphorus, it is redistilled, using an upright bulbed tube, the distillation being continued for an hour after phosphorescence has ceased to appear; the new distillate is treated with silver nitrate, &c., and also is tested for phosphorus by oxidising with chlorine-water and adding ammonium molybdate.

In examining for alkaloïds, special care must be taken not to mistake ptomaïnes for other alkaloïds, and to allow for the impure form of the latter. The material is treated with alcohol containing tartaric acid, the extract filtered, evaporated, dissolved in water, filtered, neutralised with potash, concentrated, treated with alcohol, separated from the potassium tartrate, and the neutral aqueous solution is tested with alkaloïd reagents (a preliminary test with tartaric acid and iodic acid being made for morphine) and examined systematically if required. A portion is rendered alkaline, and steam-distilled for nicotine, coniine, aniline, &c. In the absence of these volatile bases, another portion is extracted with ether successively when neutral, acid, and alkaline, then with chloroform while still alkaline, and finally is made ammoniacal and extracted with amyl alcohol. The third portion is reserved for the direct confirmatory examination of any alkaloïd indicated in the other portions. The aqueous residue is tested for narceine and curarine, whilst the various extracts are examined separately. The residue from the alkaline-ether extract is tested with phosphoric acid for aconitine. Vitali's atropine reaction is liable to be hidden by xanthoproteïn colour reactions. For strychnine, a double test is made: first, a drop of vanadic acid solution is mixed with the residue, dissolved in sulphuric acid, which is subsequently diluted with concentrated sulphuric acid, and then solid ammonium vanadate is dusted over another portion of the same solution. Attention is called to the fact that colocynthine gives reactions with both vanadic and chromic acids, which resemble those of strychnine with the same reagents. The amyl alcohol extract, after purifying, serves for confirming the presence of morphine.

Another portion of the original extract is examined for metallic poisons soluble in alcohol. The examination for metallic poisons generally is made with the residue from the first distillation or that from the alcoholic extraction; in the latter case the alcohol is expelled by warming. The residue is heated with hot water, potassium chlorate, and hydrochloric acid until the organic tissue is destroyed and all chlorine driven off, the magma is treated with tartaric acid, then largely diluted with water and, after 24 hours, filtered. The insoluble portion is treated (if required with more chlorate and hydrochloric acid, then) with alcohol, and with ether to extract fat, and is ignited. The ash is treated with very dilute hydrochloric acid, and the residue dried, ignited, weighed, and proved conclusively to be silica by fusion with sodium carbonate; or is examined for silver, lead, barium, and strontium. The soluble portion is made up to a definite volume, and must be free from chlorine and chloric acid.

For mercury, a portion is nearly neutralised by means of potash, and is digested with brass wool for 15 minutes at 70°; if the brass is visibly amalgamated, the presence of mercury is confirmed by heating in a test-tube, &c.; but when the presence of mercury is not so evident, the brass wool is burnt with copper oxide in a current of air in a tube 25 cm. long, drawn out to a doubly bent capillary, in which any mercury is accumulated, and identified with iodine. To estimate mercury, the hot hydrochloric solution is treated with hydrogen sulphide, the precipitate collected on an asbestos filter (or if arsenic is present, it is first digested with yellow ammonium sulphide) washed with hydrochloric acid, dissolved in nitric acid, filtered through some asbestos, and the washings and filtrate diluted and treated with phosphorous acid. After 24 hours, the calomel is filtered off, washed with, water, alcohol, and ether, and weighed on a tared filter. Throughout the estimation, high temperatures and contact with organic matter are to be avoided.

To detect antimony, some of the liquid partly neutralised with ammonia is placed in a bright platinum dish with a piece of zinc for six hours; the brownish-black antimony flakes obtained in this manner being more trustworthy than Marsh's test. This test does not answer in the presence of tin; but by fusing the mixed oxides with sodium hydroxide, most of the tin can be separated. To estimate antimony, hydrogen sulphide is passed through the slightly acid, and at first boiling, solution until it has cooled down; after three days, most of the hydrogen sulphide is driven off by carbonic anhydride, the precipitate washed with an acetic acid solution of ammonium acetate, treated and washed with a solution of sodium sulphide, containing hydrogen sulphide, the solution treated carefully with hydrochloric acid, warmed, and then boiled. After 24 hours, the precipitate is collected, treated with an acetic acid solution of ammonium acetate, then carefully with nitric acid, evaporated, the residue moistened with sodium hydroxide, intimately mixed with dry sodium carbonate, dried, introduced by small quantities at a time into fused sodium nitrate in a silver crucible, and the mass, when cold, treated with water. After 24 hours, the precipitate is washed with 45 per cent. alcohol, containing soda, digested with a hot solution of tartaric and hydrochloric acids for half an hour, filtered, and washed with a dilute solution of tartaric and hydrochloric acids. The filtrate and washings combined are concentrated in a water-bath, the excess of acid reduced with ammonia, and the antimony precipitated by hydrogen sulphide as a pure orange-coloured sulphide which is converted into oxide by Bunsen's method. The purity of the antimony is ultimately confirmed by its volatility.

To detect arsenic, mercury and antimony being absent, various obvious precautions are observed in applying the Marsh test to some of the liquid, and when a mirror is obtained, the tube containing it is divided by a diamond into four parts, of which one is used for the odour test, another for solubility in freshly-prepared sodium hypochlorite, a third for dissolving in nitric acid and testing with silver nitrate, whilst the fourth is dissolved in nitric acid, and converted into arsenic sulphide by colourless ammonium sulphide. To estimate arsenic, hydrogen sulphide is passed through the warm hydrochloric solution for 12 hours, and after remaining three to five days in a closed flask, most of the hydrogen sulphide is driven off by a current of carbonic anhydride; the procedure then resembles that described in the antimony estimation, but various points are to be observed:—1. Ammonia or ammonium carbonate are the only solvents used for arsenic sulphide on the filter. 2. The fusion is conducted in a porcelain crucible with fusion mixture and potassium nitrate. 3. The arsenic is always weighed as magnesium pyroarsenate. 4. The alkaline solution is not precipitated directly with magnesia mixture, but is first submitted to the following treatment:—Neutralisation with nitric acid, expulsion of carbonic anhydride and nitrous acid, precipitation with hydrogen sulphide, and conversion into arsenic acid. 5. The ammonium magnesium arsenate is redissolved in hydrochloric acid and reprecipitated by ammonia. 6. Small quantities of magnesium arsenate are converted into pyroarsenate by dissolving in very dilute nitric acid, evaporating in a porcelain crucible over a water-bath, and carefully and gradually igniting the residue; the method is susceptible of great accuracy; as little as 0·0093 to 0·0077 gram of arsenic in a portion of a dead body has been estimated. 7. Large quantities of pyroarsenate are preserved as such for reference; small quantities are converted into metallic arsenic in a Marsh's apparatus, and are preserved in a sealed tube.

In the absence of mercury, antimony, and arsenic, the hydrochloric acid solution is made alkaline with soda, acidified with acetic acid, hydrogen sulphide passed in at the boiling point of the liquid and until cold, sodium carbonate added to distinct alkalinity, and the whole allowed to remain corked up until clear. The solution serves for detecting and estimating tin. The precipitate is washed with sodium sulphide containing hydrogen sulphide, oxidised with nitric acid, evaporated, moistened with sodium hydroxide, mixed with fusion mixture, dropped into molten nitre in a silver crucible, extracted with water, supersaturated with hydrochloric acid, filtered, and the hydrochloric acid solutions submitted to the ordinary methods of analysis, weighing any metal isolated in a definite form. The separation of iron, alumina, and zinc in the presence of calcium and magnesium phosphates is effected in the following manner:—The hydrochloric acid filtrate from the hydrogen sulphide precipitate is concentrated on the water-bath, treated with chlorine-water, evaporated, the residue dissolved in very dilute hydrochloric acid, filtered, the solution supersaturated with ammonia, excess of the latter nearly expelled on the water-bath, the precipitate removed, the solution acidified with acetic acid, and hydrogen sulphide passed into the boiling hot liquid until it gets cold. The zinc sulphide is weighed. The ammonia precipitate is dissolved in nitric acid, treated in a platinum dish with tin, which by repeated and careful treatment with nitric acid is converted into stannic oxide, and with it the phosphoric acid into insoluble stannic phosphate, from which the alumina is washed out by very dilute nitric acid, and estimated in the solution by precipitating with ammonia, igniting the precipitate, fusing the ignition residue with sodium carbonate, extracting with water, filtering, &c. The alkaline filtrate from the hydrogen sulphide precipitate is examined for tin :—It is acidified with hydrochloric acid, boiled, hydrogen sulphide passed through until it is cold; after remaining for 24 hours in a warm place the precipitate is collected, washed with an acetic acid solution of ammonium acetate, and ignited with the filter. The residue is moistened with nitric acid, evaporated, ignited, and to get rid of the iron present it is washed into a silver crucible, dried, and treated for half-an-hour with molten sodium hydroxide, extracted with water, filtered, the filtrate acidified with hydrochloric acid, and the tin obtained in the usual manner.

In conclusion, it is pointed out that not only are potassium, sodium, calcium, magnesium, iron, and manganese normally present in the human body, but that aluminium, copper, and zinc are always met with, and less frequently tin and lead. These extraneous metals are derived from food, cooking utensils, medicine, &c.; aluminium comes from various sources, and even after death may be introduced in the dust, when the post-mortem takes place in the country. The author in advocating his employment of a solution prepared directly from the corpse material for the detection of arsenic, points out that considering the sensitiveness of the arsenic reaction a concentration of the solution is not necessary, that the "brown speck" on the porcelain lid referred to by Otto cannot interfere in his method, which, moreover, obviates any chance of vitiation through arsenical hydrogen sulphide. It is also shown that the presence of chlorides and nitrates does not stop the formation of gaseous hydrogen arsenide, provided that the zinc and hydrochloric acid are in excess and the evolution of hydrogen is allowed to proceed sufficiently long; but the presence of free nitric acid stops the evolution temporarily. It is still doubtful whether solid hydrogen arsenide is converted into the gaseous modification by zinc and hydrochloric acid.

Ordinarily only one poison is found in a corpse, but nevertheless it should be borne in mind that there is the possibility of more than one being present. D. A. L.

Detection of Paraffin in Beeswax. By H. HAGER (*Zeit. anal. Chem.*, **29**, 480—481; from *Pharm. Centralhalle*, **30**, 565).—A few grams of the substance in fine, air-dried shavings is gradually heated in a small, porcelain capsule, until fumes begin to rise. A half-litre wide-mouthed bottle is then inverted upon the capsule, and when filled with white vapours is closed and set aside until the fumes have condensed upon its walls. The sublimate is then dissolved in 3 c.c. of chloroform, the chloroform evaporated in a test-tube, and the residue boiled with 4 c.c. of soda solution. If paraffin was present, it will after cooling be found floating on the clear solution. A drop of the chloroform solution may also be evaporated on a slip of glass and examined microscopically.

The fumes from pure beeswax are not so white as from paraffin, and are only obtained at a higher temperature (300—320°). The sublimate gives a coloured solution with chloroform, and a coloured and turbid solution with soda. The residue from the chloroform solution is a dull film; paraffin on the contrary gives separate grains in a clear field. M. J. S.

Condition of the Sulphuric Acid in Plastered Wines, and a Method of Distinguishing between Plastered Wines and Wines mixed with Sulphuric Acid. By L. Roos and E. Thomas (*Compt. rend.*, **111**, 575—577).—Wines which have been mixed with calcium sulphate do not contain potassium hydrogen sulphate. The liberated tartaric acid interacts with the organic potassium compounds in the wine, and forms a new quantity of potassium hydrogen tartrate. Direct experiment shows that when calcium sulphate is added to a solution of potassium hydrogen tartrate, and an acetate, malate, citrate, or succinate, the liquid contains no free sulphuric or tartaric acid, but acetic, citric, malic, or succinic acid is liberated. No potassium hydrogen sulphate could be detected in plastered wines by the following method, which will detect the addition of 0·25 gram of sulphuric acid per litre.

The proportion of chlorine and the total sulphuric acid in the wine are estimated. 50 c.c. of the wine is mixed with a small quantity of ammonium acetate, and exactly precipitated with a standard solution of barium chloride. The filtrate is evaporated to dryness, heated gently, and the chlorine in the residue is estimated. If only normal potassium sulphate is present, the reaction is $K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl$, and the chlorine in the residue should be equal to the chlorine of the barium chloride, plus the chlorine originally present in the wine; if the acid sulphate is present, the reaction is $KHSO_4 + BaCl_2 = BaSO_4 + HCl + KCl$, and the free hydrogen chloride is expelled in the process of evaporation, the loss increasing with the quantity of hydrogen-sulphate present. C. H. B.

Estimation of Dissolved Solids in Wine. By E. László (*Chem. Zeit.*, **14**, 438, 455).—Results are quoted, showing the unsatisfactory character of estimations of "extractives" made by drying residues for 2½ hours. The author suggests determining the alcohol both by distillation and by an alcoholometer at 15°; the difference between the two observations being due to the "extractives" present may be utilised as a measure for them, and he finds that multiplying this difference by 0·32 gives numbers for the quantity of dissolved solid matter in 100 c.c. of wine concordant with actual determinations. The alcoholometer should not have a greater range than 10°, or at the outside 12°, and for wines of sp. gr. greater than 1·000, a saccharometer showing volume percentages is employed. D. A. L.

Detection of Methylated Nitrous Ether. By J. Muter (*Analyst*, **15**, 48).—Much of the sweet spirits of nitre in commerce is prepared from methylated spirit instead of from pure ethyl alcohol as prescribed in the pharmacopœia. The two may be discriminated by dissolving a fragment of solid potash in a sample. The methylated ether darkens, the colour varying from deep-yellow to orange-red, while the odour of methylated spirit becomes very distinct. The ether from pure spirit loses its odour of ethyl nitrite, and retains only that of ethyl alcohol, and it does not darken beyond the faintest straw colour. On treating with Hubl's reagent the distillate obtained after digestion with potash, the methylated sample will absorb 0·4 to 0·7 per cent. of iodine, but that from pure spirit none.

M. J. S.

Analysis of Carbolic and Sulphurous Disinfecting Powders. By J. MUTER (*Analyst*, **15**, 63—68).—The author calls attention to the ambiguities in the usual forms of specification for disinfecting powders. Whilst the contracts are nominally for "carbolic acid," it is commonly understood that the powder may contain chiefly cresol and other high-boiling tar phenols. There have, however, been cases where the supply of the more costly absolute phenol has been insisted on. The omission of the word "available" before "sulphurous acid" sometimes renders a literal compliance with a specification impossible.

For the estimation of the phenols, the author still employs his own process (Abstr., 1888, 92), with the single modification that 150 c.c. of a 10 per cent. solution of sodium hydroxide is now used instead of 200 c.c. of a 5 per cent. solution. The cresol, measured in contact with brine, retains about 5 per cent. of water. Since anhydrous cresol increases in volume by about 5 per cent. when shaken with 3 volumes of brine, whilst that containing water does not increase or may even diminish, this furnishes a rough but ready test for the presence of water. For more accurate work the water must be distilled out. Naphthalene, which is usually present in commercial cresol, may be estimated as follows:—50 c.c. is shaken with 200 c.c. of a 10 per cent. solution of sodium hydroxide. The phenols dissolve, leaving the naphthalene floating. The solution is removed, the naphthalene washed with a 5 per cent. soda solution, then rapidly filtered off. It is rinsed from the filter with water and again collected on a pair of filters. After drying as far as possible by pressing between blotting paper, the filters are separated and the inner one with its contents is weighed, using the outer one as a tare.

For estimating the available sulphurous acid, 2 grams of the powder is washed on a filter with dry ether until the phenols and tarry matters are removed. As soon as the ether has evaporated, the contents of the filter are thrown into a bottle containing 50 c.c. of N/10 iodine solution, and after half an hour the residual iodine is titrated by thiosulphate. This method is unsatisfactory when the basis of the powder is lime.

In sulphurous powders which have undergone oxidation, the amount of original sulphurous acid cannot be ascertained if the mixture had consisted of gypsum and calcium sulphite, but where the basis is silica, the sulphates present may be regarded as oxidised sulphites, and where sodium hydrogen sulphite has been mixed with gypsum, the estimation of calcium, sulphuric, and sulphurous acids in an aqueous extract will give the necessary data. M. J. S.

Detection of Diresorcinol as an Impurity in Synthetically Prepared Phloroglucinol. By J. Herzig and S. Zeisel (*Monatsh.*, **11**, 421—423).—The presence of diresorcinol, as an impurity in phloroglucinol, scarcely affects its melting point, or the numbers obtained on estimating carbon and hydrogen. It may be best detected by dissolving a few milligrams of the sample in about 1 c.c. of concentrated sulphuric acid, adding 1—2 c.c. of acetic anhydride, and warming the mixture for a few minutes in a water-bath. If diresorcinol—or its tetrethyl ether or tetracetyl derivative—be present, a bluish-violet colour, which disappears on the addition of much water or of an excess of alkali, will be produced. By this means, the presence of 0·4 per cent. of diresorcinol may be clearly shown, and the delicacy of the test is probably much greater. G. T. M.

Estimation of Sugars by means of Copper Potassium Carbonate Solution. By H. Ost (*Ber.*, **23**, 3003—3011; compare Abstr., 1890, 1031).—A solution containing 23·5 grams of crystallised copper sulphate, 250 grams of potassium carbonate, and 100 grams of hydrogen potassium carbonate per litre has the following advantages over Fehling's solution for the gravimetric determination of sugars:—(1) It is unchanged by keeping. (2) Its action on cane-sugar is relatively slight. (3) After 10 minutes boiling, the precipitation of cuprous oxide is practically complete, and thus more concordant results are obtained. (4) The monosaccharoses precipitate almost twice as much cuprous oxide from this solution as from Fehling's solution. (5) The quantity of precipitate obtained from different kinds of sugars varies considerably, thus rendering it possible to determine the composition of mixtures. The solution may also be employed for volumetric estimations, as the end reaction is sharp; the time required for boiling, is, however, longer than with Fehling's solution. For gravimetric determinations, 50 c.c. of the copper solution is mixed with 25 c.c. of the sugar solution, water is added and the liquid boiled for 10 minutes, filtered through an asbestos filter, and the cuprous oxide reduced in a stream of hydrogen. The following table shows the quantity of copper precipitated by different sugars:—

Copper.	Invert-sugar.	Dextrose.	Levulose.	Galactose.	Arabinose.
Milligrams.	Milligrams.	Milligrams.	Milligrams.	Milligrams.	Milligrams.
50	15·2	15·6	14·7	17·4	17·0
55	16·6	17·0	16·1	19·1	18·6
60	18·0	18·5	17·5	20·8	20·3
65	19·4	19·9	18·9	22·5	21·9
70	20·8	21·4	20·3	24·2	23·5
75	22·3	22·9	21·7	25·9	25·1
80	23·7	24·4	23·0	27·6	26·7
85	25·2	25·8	24·3	29·3	28·3
90	26·6	27·3	25·7	31·1	29·9
95	28·1	28·8	27·1	32·8	31·5
100	29·5	30·3	28·5	34·5	33·1

Copper.	Invert-sugar.	Dextrose.	Levulose.	Galactose.	Arabinose.
Milligrams.	Milligrams.	Milligrams.	Milligrams.	Milligrams.	Milligrams.
105	31·0	31·8	29·8	36·2	34·7
110	32·4	33·3	31·2	38·0	36·3
115	33·9	34·8	32·6	39·7	37·9
120	35·3	36·3	34·0	41·4	39·5
125	36·8	37·8	35·4	43·1	41·1
130	38·2	39·3	36·8	44·8	42·8
135	39·7	40·8	38·2	46·5	44·4
140	41·1	42·3	39·6	48·3	46·0
145	42·6	43·8	41·0	50·0	47·6
150	44·0	45·3	42·5	51·8	49·3
155	45·5	46·8	43·9	53·6	50·9
160	47·0	48·3	45·3	55·4	52·6
165	48·5	49·8	46·7	57·2	54·3
170	50·0	51·4	48·1	59·0	55·9
175	51·5	52·9	49·5	60·8	57·5
180	53·0	54·5	51·0	62·7	59·2
185	54·5	56·0	52·5	64·5	60·9
190	56·0	57·6	54·0	66·4	62·7
195	57·5	59·2	55·5	68·3	64·4
200	59·1	60·8	57·0	70·3	66·2
205	60·7	62·4	58·6	72·3	68·0
210	62·4	64·1	60·2	74·3	69·8
215	64·1	65·8	61·8	76·3	71·6
220	65·8	67·5	63·5	78·3	73·5
225	67·5	69·2	65·2	80·3	75·4
230	69·3	70·9	66·9	82·4	77·3
235	71·1	72·7	68·7	84·5	79·3
240	72·9	74·5	70·6	86·6	81·3
245	74·8	76·4	72·5	88·9	83·4
250	76·7	78·4	74·4	91·2	85·5
255	78·6	80·5	76·5	93·5	87·6
260	80·5	82·8	78·8	95·9	89·8
265	82·5	85·1	81·1	98·3	92·2
270	84·7	87·5	83·5	100·7	94·6
275	87·1	89·9	85·9	103·3	97·1
280	89·7	92·4	88·6	106·1	99·6
285	92·3	94·9	91·3	109·0	102·3
290	95·1	97·6	94·2	112·0	105·1
295	98·0	100·4	97·2	115·1	107·9
298·7	100·0	102·5	99·0	117·0	109·5

In the case of lactose, the factor copper/lactose = 1·51 to 1·57 for solutions containing from 125 to 198 milligrams of sugar. For volumetric work, an indicator must be employed; after 20 minutes boiling, 198 milligrams of lactose precipitate 190 milligrams of copper.

Raffinose, $C_{18}H_{32}O_{16} + 5H_2O$, does not affect the copper solution, but after hydrolysis, it has the highest reducing power, 50 milligrams precipitating 150 milligrams of copper. J. B. T.

Estimation of Sugar in Milk. By M. Kühn (*Bied. Centr.*, **19**, 628; from *Milchzeit.*, **18**, 926).—Results obtained by Tollens' method agree better with those obtained by Soxhlet's method, when only so much serum solution is employed that the colour is bluish after boiling. If so much sugar solution is used that the liquid is greenish after reduction, results will be obtained which are 0·1 to 0·15 per cent. too low. The phosphotungstic acid method is not recommended. If Soxhlet's method is not used, the lead acetate method should be employed. N. H. J. M.

Estimation of Ash in Raw Sugar. By W. Minor (*Chem. Zeit.*, **14**, 510).—Stammer objects to the use of oxygen, and recommends air for the incineration of raw sugar in estimations of ash. The author has investigated the point, and sees no reason for disqualifying oxygen nor any special virtue in the atmospheric nitrogen, and as burning the charred sugar in oxygen takes 25 minutes, whilst combustion in air, with the aid of mechanical agitation, requires from 6 to 15 hours, he considers the oxygen method is distinctly to be recommended. D. A. L.

Estimation of Starch. By O. Reinke (*Zeit. anal. Chem.*, **29**, 472—475; from *Zeit. Spiritindust.*).—The author divides the processes hitherto proposed into those with and without high pressure, and recommends the following as the best of the respective methods :—*With high pressure:* 3 grams of the finely ground substance is stirred with 25 c.c. of a 1 per cent. solution of lactic acid and 30 c.c. of water in a metallic beaker, then covered and heated for 2½ hours in a digester (Soxhlet's or Lintner's) at 3½ atmospheres pressure, then mixed with 50 c.c. of hot water and, after cooling, made up to 250 c.c. and filtered. 200 c.c. is then inverted by cohobating with 15 c.c. of hydrochloric acid (1·125 sp. gr.) for 2½ hours, then neutralised with soda, made up to 500 c.c., and 25 c.c. of it titrated with Fehling's solution. *Without high pressure:* 3 grams of the substance is boiled with 50 c.c. of water, and then digested for an hour at 62·5° with 0·05 gram of Lintner's diastase. It is then cooled, made up to 250 c.c., and 200 c.c. inverted with acid as above. For the preparation of Lintner's crude diastase, 1 part of green malt is extracted for 24 hours with 2 to 4 parts of 20 per cent. alcohol. The extract, filtered by suction, is precipitated with twice, or at most 2½ times, its volume of absolute alcohol. The upper liquor is poured off and the precipitate thrown upon a pressure filter, then rubbed down with absolute alcohol in a mortar, again filtered and washed with absolute alcohol and then with ether, and finally dried in a vacuum over sulphuric acid. For the purification of this raw product, the precipitation and digestion with alcohol, washing with ether, and drying are repeated. By this means, albuminoïd impurities are rendered insoluble and dextrinoïd extractive matters removed. The dried product is a loose, yellowish-white powder, which has no action on

Fehling's solution either before or after boiling with hydrochloric acid, and which does not turn brown when its solution is evaporated on the water-bath. It exhibits great hydrolytic activity.

M. J. S.

A New Application of Molisch's Reactions. By G. Colasanti (*Gazzetta*, **20**, 299—305).—Molisch (Abstr., 1886, 923) found that the merest traces of sugar or glucosides (0·00001 per cent.) could be detected by the addition of one or two drops of an alkaline solution of α-naphthol or thymol (15 to 20 per cent.), together with an excess of concentrated sulphuric acid. Molisch further derived from this reaction a confirmation of the alleged presence of sugar in normal urine.

The author finds that extremely dilute solutions of potassium or sodium thiocyanate, treated in the same manner, show first a green band and, on agitation, an intense violet coloration resembling in all respects that obtained from solutions of sugar. On cooling the liquid, a compound containing the naphthalene nucleus and the sulphonic group separates in a mass of long, slender needles. The solution of thiocyanate or thiocyanic acid must be very dilute, or on addition of sulphuric acid a brown coloration is produced, and hydrogen sulphide is evolved. Urine must similarly be diluted before treatment with α-naphthol, and altogether fails to give the thymol reaction.

As urine has been found to contain thiocyanic acid, Molisch's reaction affords no confirmation of the presence of sugar in that fluid.

S. B. A. A.

Reaction of Thiocyanic Acid. By G. Colasanti (*Gazzetta*, **20**, 306—308).—If a few drops of a solution of auric chloride ($\frac{1}{10}$th per cent.) made alkaline with a saturated solution of sodium carbonate or a 5 per cent. solution of potash are added to a few c.c. of a dilute solution of a thiocyanate (0·01 per cent.), a deep violet coloration is obtained, and a precipitate of metallic gold gradually separates. The thiocyanic acid in urine does not give the reaction, the liquid merely acquiring a reddish coloration. S. B. A. A.

Schneider's Method for the Estimation of Malic Acid in Wine. By E. Niederhäuser (*Chem. Centr.*, 1890, ii, 172; from *Pharm. Centralhalle*, **31**, 378—379).—100 c.c. of the wine is neutralised with decinormal alkali, evaporated, incinerated, and the carbonic anhydride in the ash determined. From this amount, the quantity of carbonic anhydride equivalent to the total tartaric acid present is deducted, the difference being then calculated into malic acid. Since, however, wines usually contain other substances (tannic, succinic, acetic acids), all of which neutralise alkalis, and would when incinerated produce carbonates, the author considers the method valueless. J. W. L.

Comparison between Methods for Estimating Tartaric Acid. By J. Tóth (*Chem. Zeit.*, **14**, 63—64).—To compare the three rival methods for the estimation of tartaric acid, the "original Goldenberg" method, the "Lorenz-Goldenberg" method, and the "modified Goldenberg" method, the author made simultaneous and duplicate estimations in crystalline calcium tartrate, in wine lees, in argol, and in tartaric acid, following rigidly the directions laid down in each method; the numbers obtained are tabulated, and from the results it is concluded that the Lorenz modification of the Goldenberg method is the best method, and is applicable in all cases, a specially valuable factor about it being the introduction of one-third normal soda for the titration. With regard to Boessneck's suggested method, the author shows that the amount of antimonious oxide taken up by the calcium tartrate is not $\frac{1}{2}$ a mol. for 1 mol., but is a variable quantity, which seems to depend on the amount of free tartrate in solution.

D. A. L.

Estimation of Tartaric Acid. By J. Wolfmann (*Chem. Zeit.*, **14**, 220; compare Tóth, preceding abstract).—The author considers the use of litmus tincture unsatisfactory in deeply coloured tartaric solutions; he has noticed neutralisation of alkali by humus in such solutions, and does not regard the question of the estimation of tartaric acid as solved by the Lorenz method, in fact, looks with greater favour on the Goldenberg-Geromont results. He himself endeavoured unsuccessfully to determine tartaric acid by titration with permanganate. D. A. L.

Estimation of Tartaric Acid in the Crude Products of Tartaric Acid Factories. By J. Telbisz (*Chem. Zeit.*, **14**, 347).—In consideration of results recently published by Tóth (see above), the author has made several estimations of tartaric acid in various samples of calcium tartrate and dried wine lees, applying, with much precision, both the "original" and "modified" Goldenberg-Geromont, and also the Lorenz method; the results are tabulated, and in his hands the latter method yielded undoubtedly higher results than the first two methods, and he agrees with Wolfmann (preceding abstract) in considering the modified Goldenberg-Geromont method the most trustworthy, up to the present time. Variations as great as 7—10 per cent., noted by Tóth, in different estimations of the same sample by this method, have not been observed in the present experiments.

D. A. L.

Estimation of Citric Acid in Parts of Plants. By E. Claassen (*Zeit. anal. Chem.*, **29**, 468—469).—The plant is extracted with very dilute ammonia and ammonium carbonate, the liquid somewhat concentrated, precipitated with lead acetate, and filtered. The dried precipitate is boiled out with strong alcohol, then suspended in water, and decomposed by hydrogen sulphide. The filtrate is evaporated to a thin syrup, mixed with ammonium chloride, excess of ammonia, and calcium chloride, and 3 volumes of alcohol added. The precipitate is filtered, washed with 75 per cent. alcohol, dried, and dissolved in hot dilute hydrochloric acid. After cooling, it is filtered, treated with excess of ammonia, and again filtered, and evaporated on the water-bath to dryness. The residue is taken up with boiling ammoniacal water, and the insoluble calcium citrate collected on a weighed filter. Traces of citrate in the filtrate may be recovered by repeating the evaporation. M. J. S.

Amount of Volatile Fatty Acids in Rancid Butter. By P. Corbetta (*Chem. Zeit.*, **14**, 406).—Samples of fresh butter were taken and examined on the 16th of February for volatile fatty acids; they were then exposed in vessels covered with paper, and again examined on April 3rd, when, in all cases, a reduction in the quantity of volatile fatty acids was observed; in a subsequent examination on April 30th, no further change was noted, but a final test, on August 9th, indicated a still further falling off in these acids. The disappearance of volatile fatty acids in the rancid butter, although progressive in these experiments, was in no instance very considerable, and in no case could volatile fatty acids be washed from the rancid butter either by water or sodium hydrogen carbonate. D. A. L.

Butter and Margarine. By C. Violette (*Compt. rend.*, **111**, 345—347).—The acids resulting from the saponification of 50 grams of pure, dry butter by aqueous potash are distilled in a current of steam, and the successive portions of the aqueous distillate (the total volume of which should not be less than 10 litres) are titrated with normal sodium hydroxide, using phenolphthaleïn as an indicator. The volatile acids, which solidify, and the non-volatile acids also, are weighed, after being dried in a vacuum and melted. A table is given showing the results obtained with various butters and with margarine. It is assumed, on the evidence of Duclaux's results, that the ratio between butyric and caproic acids in genuine butter remains constant, and equal to 1·645.

In ordinary butters the mean proportion of volatile acids is 7·6 per cent., with a minimum of 7·0, and the proportion of non-volatile acids is 84·0 per cent., with a maximum of 84·6. In the case of a butter of high quality, the addition of about 20 per cent. of margarine would lower the proportion of volatile acids from 8·5 to the minimum of 7 per cent., and would raise the non-volatile acids from 82·63 to 84·76. In the case of ordinary butter, the addition of 9 per cent. of margarine would reduce the volatile acids to 7 per cent.

C. H. B.

Optical Analyses of Butters. By C. Violette (*Compt. rend.*, **111**, 348).—From his observations, the author concludes that butter and margarine have different indices of refraction, the deviations in the oleorefractometer being $-33°$ to $-27°$ for butters, and $-15°$ to $-8°$ for margarines. The indications of the oleorefractometer are sufficiently exact when the instrument is applied to mixtures of constituents giving known deviations. It is necessary to ascertain, by means of a large number of observations, the minimum deviation below which a butter may be regarded as adulterated with margarine. The oleorefractometer may be used for the analysis of commercial butters, but its indications will not be very exact, because these butters will give deviations below the minimum for good butters, and the proportion of margarine deduced from the results will be too low.

C. H. B.

Analysis of Lard, Cotton Oil, and Tallow. By J. Muter and L. de Koningh (*Analyst*, **15**, 48—50).—Employing the method described by themselves (*Analyst*, April, 1889) for estimating the liquid fatty acids in fats, and for treating them with iodine without exposure to air, the authors have obtained the following results. They regard tallow as the best material for the preparation of oleïc acid, and for this acid they find the iodine absorption to be 90 per cent., and to vary at most 0·2 per cent. from theory. The oleïc acid from lard never gives so low a number, the average being about 93 per cent., whilst that from cotton oil is found to be 135, with very little variation. In consequence of this wide difference, the percentage of cotton oil in a sample of adulterated lard can be indirectly estimated with considerable accuracy. M. J. S.

Beeswax. By A. Buisine and P. Buisine (*Bull. Soc. Chim.* [3], **3**, 867—873).—The authors confirm the results previously obtained by Hübl and Hebner with respect to the free, total, and combined acids of beeswax; further, they have determined the iodine numbers for this substance, and describe a process for estimating the alcohols present. This consists in the fusion of the wax with potassium hydroxide and potash lime at 250°, which causes the evolution of hydrogen proportionally to the amount of alcohols acted on, and from the residue of this experiment the hydrocarbons existing in the wax are determined by extraction with a suitable solvent. Their results for pure, dry, washed beeswax are summarised:—

M. p. 63—64°. Entirely soluble in hot chloroform.

Wax Acids.

Free acids corresponding with	19—21 milligrams KHO per gram.
” ” ”	13·5—15·5 per cent. cerotic acid.
Total acids ”	91—97 milligrams KHO per gram.
Combined acids ”	72—76 ” ” ”
” ” ”	32·85—34·67 per cent. palmitic acid

Ratio of free to combined acid 3·5 to 3·8.

Iodine Numbers.

100 parts of wax absorb 8·3—11 parts iodine; which corresponds to 9—12 per cent. oleïc acid.

Wax Alcohols.

Hydrogen liberated by fusion with KHO, 53·5—57·5 c.c. per gram.

Wax Hydrocarbons.

M. p. 49·5. Percentage 12·5—14. Iodine fixed by 100 parts of hydrocarbon 22·05. T. G. N.

Estimation of Resin in Soap. By R. Williams (*Analyst*, **15**, 81—82).—Gladding's method (Abstr., 1885, 603) yields very good results. The author prefers to work on the soap itself rather than on the acids separated from it. M. J. S.

Estimation of Camphor. By F. Foerster (*Ber.*, **23**, 2981—2989).—A number of substances now occur in commerce, consisting of nitrocellulose and camphor, and up to the present no method is known for estimating the amount of camphor which they contain. The author proposes to carry out the estimation by distilling the substances with soda solution, when the camphor readily passes over. This may be then extracted with benzene, and the specific rotatory power of the benzene solution ascertained. Detailed instructions for carrying out the reaction, and tables of the rotation of camphor in benzene solution at different concentrations and temperatures are given in the original. The results obtained are about 0·7—1·0 per cent. too low, probably owing to the difficulty of driving out the last portions of camphor.

The author finds that sublimed camphor contains a small quantity of impurity, and that for the determination of its rotatory power, high temperatures must be avoided in its preparation, and the camphor finally twice recrystallised from 50 per cent. alcohol. It then melted at 174·8—175·3°, and after six crystallisations at 176·3—176·5°, and after 10 crystallisations the solidifying point was found by Landolt's method (Abstr., 1890, 1) to be 178·7° (corr.). The boiling point of the purified camphor was 209·1° under 759 mm. H. G. C.

Estimation of Tannin in Tea. By P. MALTSCHEFFSKY (*J. Pharm.* [5], **22**, 270—271; from *Pharm. Zeit. f. Russ.*, **29**, 127).—The tannin is precipitated by means of normal copper acetate, and the excess of copper is titrated by the aid of potassium ferrocyanide solution. The copper solution contains 7·657 grams of copper oxide per litre (1 c.c. = 0·01 tannin), and its strength is controlled by evaporating a measured volume to dryness, moistening with nitric acid, heating to redness, and weighing the oxide. The ferrocyanide solution is prepared by making up to 1 litre, 100 c.c. of a saturated solution. To standardise this solution, it is added, 1 c.c. at a time, to 5 c.c. of the copper solution diluted to 100 c.c., until a drop of the mixed liquids gives a blue colour with a solution (1 : 100) of ferric chloride. A second assay, in which the additions of ferrocyanide solution are made by tenths of a c.c. towards the end, gives the exact strength of the solution. 2 grams of tea dried at 100—107° is extracted four times with 100 c.c. of boiling water each time; the filtrates are united, made up to 400 c.c.; 100 c.c. of this solution is boiled and treated with 10 c.c. of copper solution. The precipitate is filtered off, washed with hot water, and the filtrate and washings are made up to 200 c.c.; half of this is taken, and the excess of copper is determined approximately by means of the ferrocyanide solution; the second half of the solution then serves for the exact determination of the copper. In 14 samples, the amount of tannin varied from 6·10 to 11·08 per cent. The water varied from 5·59 to 12·48 per cent.; ash, 3·14 to 9·25; aqueous extract, 17·3 to 39·4; caffeïne, 1·09 to 2·88 per cent. J. T.

Estimation of Urea. By P. MIQUEL (*Compt. rend.*, **111**, 501—502).—Many of the urophagic microbes, and especially micrococci and sarcinæ, can develop in a neutral and even in a slightly acid cultivation fluid. Several grow solely at the bottom of the vessels and produce more or less granular deposits without rendering the liquid turbid, whilst at the same time they produce a large quantity of the soluble ferment (this vol., p. 100). These clear liquids should be used for the estimation of urea.

An aqueous solution of urea is simply mixed with the cultivation fluid containing the ferment; the alkalinity is at once estimated by titration, and the liquid is heated at 50° for two hours in a well-closed vessel, which it nearly fills. The alkalinity is again determined, and from the quantity of ammonium carbonate formed the amount of urea present is calculated.

Urine and other organic liquids are previously heated with a slight excess of ammonium carbonate, filtered if necessary, and then mixed with the ferment, the object of this treatment being to prevent loss of ammonia from formation of double salts, neutralisation of any acid present, &c.

A quantity of urea exceeding 10 per cent. interferes with the activity of the ferment, and in solutions of 30 per cent. the ferment is inactive. Concentrated solutions must, therefore, be diluted. Ammonium carbonate, sodium chloride in small proportion, uric acid, ammoniacal and alkaline salts, extractive matters, albumin, and sugar in large quantity do not interfere with the results. C. H. B.

Simple Mode of Estimating Urea. By C. W. HEATON and S. A. VASEY (*Analyst*, **15**, 106—107).—The method, which does not aim at great accuracy, is suggested for the use of medical men in cases where none of the special forms of apparatus is available. An 8-ounce bottle is fitted with a thistle funnel and gas delivery tube which dips under water in a basin. In the bottle is placed 1 fluid drachm of bromine and 10 fluid drachms of a 40 per cent. solution of caustic soda. A bottle full of water is inverted over the delivery tube to receive the gas; 2 fluid drachms of urine is then poured into the generator and rinsed in by 1 fluid drachm of water, and the bottle is shaken until gas ceases to be evolved. The receiver is then closed by the thumb, removed from the basin, placed in an upright position, and filled up with water, the volume required being noted. Deducting 200 minims for the volume of air displaced by the urine and water introduced into the generator, the remainder is equal in volume to the nitrogen evolved, and each 100 minims corresponds with 0·25 per cent of urea. M. J. S.

Rapid Method of Estimating Urea in Urine. By C. J. H. WARDEN (*Analyst*, **15**, 201—203).—The apparatus is a modified Crum's nitrometer, 630 mm. long and of about 75 c.c. capacity. Into its lower end is ground a stopper, on which 10 narrow grooves have been filed. The cup above the stopcock is of 5 c.c. capacity, and is accurately marked at 2·5 c.c. The tube is graduated to show percentages of urea at once, assuming that 1 per cent. of urea in 2·5 c.c. of urine will yield 9·27 c.c. of gas. The hypobromite solution is stated to be made by dissolving 100 "grains" (? grams) of caustic soda in 750 c.c. of water and adding 25 c.c. of bromine. The inverted tube is filled with this solution and the stopper inserted. Its exterior and the cup are then rinsed and dried. It is stood in a vessel of brine and the stopper is removed. 2·5 c.c. of urine is then placed in the cup and there mixed with its own volume of saturated brine to increase its density, and this mixture is allowed to enter the tube in small portions. The last traces are rinsed in by brine. The tube is then grasped by the right hand, the thumb being tightly pressed against the open end, and the contents thoroughly agitated. It is then transferred to a vessel of water, where the heavy solutions flow away, and the volume of the nitrogen is read in the usual manner. M. J. S.

Estimation of Theïne in Tea. By G. L. SPENCER (*Chem. Centr.*, 1890, ii, 172; from *J. Amer. Chem. Soc.*, **4**, 158).—2 to 3 grams of the finely ground tea is extracted in a small beaker seven times with boiling water, the extract being each time decanted off, and the residue finally transferred to a filter, and washed with a few c.c. of boiling water. Basic lead acetate is added to the extract, about 8 c.c. usually being sufficient; the precipitate is filtered, washed with hot water, and the lead separated as sulphide, after which the filtrate is concentrated to about 50 c.c., with addition of about 5 grams of calcium hydroxide or magnesium oxide. The liquid is again filtered, the insoluble portion extracted with hot water, and the filtrate is extracted with chloroform seven times. The chloroform extract is distilled from a tared flask, and the weight of the residual theïne recorded after drying at 75°. The method has been in use in the Department of Agriculture. J. W. L.

Estimation of Quinine. By SEATON and H. D. RICHMOND (*Analyst*, **15**, 42—43).—In solutions containing quinine bisulphate dissolved in an acid, and free from salts whose base is precipitable by baryta, the quinine may be estimated by titration. Quinine bisulphate is neutral to methyl-orange, whilst the base itself has no action on phenolphthaleïn. To 25 c.c. of the solution there are added 2 drops of methyl-orange solution (0·25 gram in a litre of water), and 2 drops of phenolphthaleïn solution (0·5 gram in a litre of 50 per cent. alcohol). Baryta solution (N/10) is then run in until the red colour changes to a brown, at which point all the free acid is neutralised. The addition of baryta is then continued until the pink colour of the phenolphthaleïn appears. As the pink colour develops slowly, care must be taken not to overstep this point. The number of cubic centimetres required for this second stage, multiplied by 0·0218, gives the weight of the hepta-hydrated quinine sulphate present. M. J. S.

Reaction for Cocaïne. By F. DA SILVA (*Compt. rend.*, **111**, 348—349).—A small quantity of cocaïne, or one of its salts, or of the residue obtained by evaporating a solution, is mixed with a few drops of fuming nitric acid of sp. gr. 1·4, evaporated to dryness on the water-bath, and the residue mixed with 2 or 3 drops of concentrated alcoholic potash. A distinct and peculiar odour, recalling that of peppermint, is developed. In Dragendorff's systematic scheme of analysis, cocaïne is found among the alkaloïds extracted by benzene from an aqueous ammoniacal solution. Of the other alkaloïds of the same group, atropine, hyoscyamine, strychnine, codeïne, and eserine give colorations when treated in the same way, and eserine also develops a disagreeable odour resembling that of phenylcarbylamine. Delphinine, brucine, and veratrine give only indistinct odours, which cannot be confounded with that from cocaïne. Sabadilline and narcotine can be recognised in the same way, but the other alkaloïds give no sensitive reactions of this order.

The reaction will detect 0·5 milligram of cocaïne hydrochloride.

C. H. B.

Detection of Colchicine in Corpses. By N. Obolonski (*Zeit. anal. Chem.*, **29**, 493).—The finely divided viscera are rubbed up with glass powder, treated with oxalic acid, and digested for 12 hours with alcohol. The liquid is squeezed out, and the dry residue twice washed with alcohol. The extract is concentrated at a temperature not exceeding 80°, and the cooled residue made up to the original volume with alcohol. The filtered liquid is evaporated as before, and this operation repeated until no clots separate on the addition of alcohol. The residue is then dissolved in water, the solution purified by shaking with light petroleum, and the colchicine finally extracted with chloroform as usual.

The alkaloïd is best identified by means of the violet colour produced by nitric acid; by Erdmann's reagent (nitrosulphuric acid), which gives in succession green, dark-blue, violet, and yellow colours, turning to raspberry-red on adding alkali; also by Mandelin's reagent (1 gram of ammonium vanadate in 200 grams of sulphuric acid) which gives a green colour. Colchicine is with difficulty destroyed by putrefaction of animal matter. The kidneys, bladder, and urine are best suited for forensic examination. M. J. S.

Detection of Bile Constituents in Urine. By A. Jolles (*Zeit. anal. Chem.*, **29**, 402—406).—Of the various tests proposed for detecting bile pigments in urine (Gmelin's, Huppert's, Vitali's, Rosenbach's, Ultzmann's, Hoppe-Seyler's, Dragendorff's), those of Rosenbach and Huppert, with the following modifications, give the best results:—

Rosenbach's Test.—A large quantity of the urine is filtered through clean, white filter-paper, the interior of the filter is touched with a drop of strong nitric acid containing nitrous acid, and the funnel is gently warmed over a flame. After a few minutes a green ring is formed round the spot moistened by the nitric acid.

Huppert's Test.—About 10 c.c. of the urine is shaken with an equal volume of milk of lime containing 10 grams of calcium oxide in the litre. The success of the test depends on the proper concentration of the milk of lime. The precipitate is filtered off and washed into a test tube with alcohol and dilute hydrochloric acid, then filtered, and the filtrate boiled. With only traces of bile pigments, the liquid becomes green to blue. An estimate of the amount of bile constituents can be obtained from the iodine number of the urine. If g

is the number of grams of iodine absorbed by 10 c.c. of the urine, and s the specific gravity, the iodine number is $\frac{1168g}{s-1}$. The number for normal urine, filtered after cooling, is 6·5 to 8·1, though even in specimens rich in uric acid it rarely exceeds 7·8. The presence of even traces of bile pigments raises the number to 9·6, and values as high as 17·4 have been observed. M. J. S.

New Test for Albumin. By A. Jolles (*Zeit. anal. Chem.*, **29**, 406—407).—About 8 or 10 c.c. of albuminous urine is mixed with an equal volume of concentrated hydrochloric acid, and then 2 or 3 drops of a saturated solution of bleaching powder deposited quietly on the surface. If as little as 0·01 gram of albumin per 100 c.c. is present, a white turbidity appears at the surface of contact. This test, being less sensitive than that with nitric acid, which latter will detect 0·0015 gram per 100 c.c., may be used to find approximately the proportion of albumin present, since by diluting the urine until the one test gives an indication but the other none, the percentage may be known to lie between the above minimum limits.

M. J. S.

Detection of Albumin in Bacterial Urines. By A. Jolles (*Zeit. anal. Chem.*, **29**, 407—408).—The most sensitive test for albumin in urine is that with acetic acid and potassium ferrocyanide, the lower limit of which is 0·0008 gram in 100 c.c. It is, however, necessary to filter the urine to obtain a standard with which to compare the turbidity produced by the test. When bacteria are present, a clear filtrate is best obtained by shaking with infusorial earth before filtering. In the case of purulent, slimy urines, rich in leucocytes, traces of albumin may adhere to the precipitate; but by washing this with warm potash, and testing the filtrate, the smallest traces of albumin may be detected. M. J. S.

General and Physical Chemistry.

Spectra of the Alkali Metals. By H. Kayser and C. Runge (*Ann. Phys. Chem.* [2], **42**, 302—320).—The alkali metals or their salts were volatilised in the electric arc, and their spectra, obtained by means of a Rowland grating, were examined. It was found that lines belonging to any one series could be expressed in terms of λ^{-1}, the reciprocal of their wave-lengths, by the formula $\lambda^{-1} = A + Bn^{-2} + Cn^{-4}$, which is a modification of Balmer's formula, and in which n is a whole number, which may vary from 3 to 16.

All the alkali metals have a number of reversible lines, which occur in pairs (except in the case of lithium), and are divided over the whole length of the spectrum; these form the chief series. The formulæ for the first lines in each series of pairs are as follows:—

Lithium....	At. wt.	7·01	$\lambda^{-1} = 43584{\cdot}73 - 133669n^{-2} - 1100084n^{-4}$.
Sodium.....	,,	22·995	$\lambda^{-1} = 41536{\cdot}81 - 129985n^{-2} - 803301n^{-4}$.
Potassium ..	,,	39·09	$\lambda^{-1} = 35086{\cdot}55 - 126983n^{-2} - 625318n^{-4}$.
Rubidium ..	,,	85·2	$\lambda^{-1} = 33762{\cdot}11 - 125521n^{-2} - 562255n^{-4}$.
Cæsium	,,	132·7	$\lambda^{-1} = 33501{\cdot}56 - 125077n^{-2} - 489885n^{-4}$.

The wave-lengths are given in Ångström units. It will be seen that all three constants in the formula decrease as the atomic weight rises. The wave-lengths, therefore, increase with rising atomic weight, as Boisbaudran has already pointed out. The difference between the values of λ^{-1} for lines in each pair is inversely proportional to the fourth power of n, the lowest value of n being always 3.

In addition to the above, there are also two series of lines for lithium, rubidium, and cæsium, which (again with the exception of lithium) form one series of pairs; and there are four series of lines for sodium and potassium, forming two series of pairs. The first lines in each pair are given by the above formula, the value of the constants being

	First Series.			Second Series.		
	A.	B.	C.	A.	B.	C.
Li........	28586	109625	1847	28666	122391	231700
Na	24476	110122	3257	24549	120726	197913
K........	21991	114450	111241	22021	119393	63243
Rb.......	20939	121193	133207	—	—	—
Cs	19743	122869	311224	—	—	—

The difference between the values of λ^{-1} for lines in the same pair is always the same for each element. It is equal to that of the first series when $n = 3$, and appears, therefore, to be characteristic for each element. The mean values of this difference are Na, 172, K, 568, Rb, 2344, Cs, 5450, in wave-numbers. These numbers are very nearly in the proportion of the squares of the atomic weights, for if their square roots be multiplied by 1·706 we get

	Na, 23·0	K, 40·6	Rb, 82·6	Cs, 126·0,
instead of	22·995	39·09	85·2	132·7.

For lithium, assuming the above law to be general, the calculated difference between the pairs is one which would quite fall within the limits of observation, but as the lithium lines do not form pairs, this metal seems to be an exception to the rule.

A comparison has been made between the lines here measured and the Fraunhofer lines in Rowland's solar atlas. Only two pairs in the chief series of sodium lines could be detected, the lines of all the other elements being apparently absent. H. C.

Dispersive Power of Organic Compounds. By R. Nasini (*Gazzetta*, **20**, 356—361).—A claim for priority as against Barbier and Roux (Abstr., 1890, 1353).

Relation between the Refractive and Rotatory Powers of Chemical Compounds. By I. I. Kanonnikoff (*J. Russ. Chem. Soc.*, **22**, 85—96).—In two previous papers (Abstr., 1888, 326, 453), the author has shown that on expressing the relation of the refractive and rotatory powers of a substance by the equation $\alpha = A\phi - B$, the relation $A/B = C$, a constant peculiar for the solvent, and independent of the optically active substance. The author has investigated solutions of camphor and turpentine in over 70 different organic solvents, and gives his results in tabular form. It is found that in homologous compounds, such as aliphatic alcohols, ethereal salts of fatty acids and their halogen derivatives, the free acids, the aldehydes, chlorides, bromides, &c., the constant C (as a mean = about 26) increases with every increase of CH_2, the differences diminishing from the lower to the higher members, and varying between 1·35 and 0·46, or, as a mean = 0·85. The difference for an increase of $H_2 = 1·4$ in genetically connected compounds, and $-2·5$ for compounds of dissimilar constitution. Similar values are found for other changes in composition and constitution (double linkage, isomerism, polymerism, substitution), but it would occupy too much space to give the results in detail. For aromatic compounds, the equation $\alpha = A\phi - B$ of the fatty series is converted into $\alpha = A\phi + B$. But where in aliphatic compounds increasing complexity in composition is regularly accompanied by an increase of the value of C, in the case of aromatic compounds a decrease is observed. The author proposes to investigate the influence of inorganic solvents on the value C. B. B.

New Photographic Method. By A. G. Green, C. F. Cross, and E. J. Bevan (*Ber.*, **23**, 3131—3133).—The diazo-compounds of dehydrothiotoluidine and its condensed derivatives, which form the dyes of the primuline group, can be employed for photographic purposes; as the sensitiveness of these compounds is increased by combination with the complex colloïds which constitute animal or vegetable textile fabrics. The sensitive surface is prepared by colouring a cotton or silk fabric with primuline (1 to 2 per cent.), and then diazotising. Such a surface will give a complete positive picture after 40 to 180 seconds exposure, that is to say, in the bright lights the diazo-compound is completely, in the half lights only partially, decomposed, so that a perfect reproduction of the original is obtained in the form of diazo-primuline. The picture can be developed with any of the various amines or phenols which form a dye with the diazo-compound.

The authors' experiments have already brought to light the following facts:—(1.) The action of light consists in the decomposition of the diazo-group, with evolution of nitrogen, probably with formation of the corresponding primuline phenol. (2.) The rapidity of the action of light varies, *cæteris paribus*, with the nature of the substance with which the diazo-compound is combined. (3.) Photographic reproductions of the spectrum show that, as regards intensity of action, the various rays of light are not in the same order as that in which they stand with reference to halogen salts of silver.

F. S. K.

Action of Borax in Developers for Photographic Plates. By P. Mercier (*Compt. rend.*, **111**, 644—645).—Borax, although an alkaline salt, acts as a retarder of development when mixed with pyrogallol or catechol. The author points out that this is doubtless due to the formation of the conjugated acids described by Lambert (Abstr., 1889, 864). Quinol, resorcinol, sodium amidonaphthol-β-sulphonate (eikonogen), and hydroxylamine hydrochloride do not form similar conjugated acids, and with these compounds borax acts as a very good accelerator of development. C. H. B.

Optical Notes. By E. Wiedemann (*Ann. Phys. Chem.* [2], **41**, 299—301). The violet colour of iodine dissolved in carbon bisulphide changes to brown when the solution is cooled by means of ether and solid carbonic anhydride (Abstr., 1888, 543). The author now finds, in accordance with a statement by Liebreich, that when the brown solutions of iodine in ethereal salts of the fatty acids are heated to about 80° they become violet, provided the solutions be not too concentrated.

Solutions of eosin or Magdala-red in alcohol, heated in capillary tubes, are found to exhibit a very marked fluorescence at temperatures above the critical. Experiments with saffranine failed owing to its decomposition. H. C.

Contact Difference of Potential of Metals. By F. Paschen (*Ann. Phys. Chem.* [2], **41**, 186—209).—The author shows that an amalgam prepared by the electrolytic deposition of zinc on mercury changes in the electromotive properties which it at first exhibits, on merely being allowed to stand for some time. In order to restore its original properties, it must be submitted to a new and longer electrolysis. Thus 705·8 grams of mercury were placed in a solution of zinc sulphate of sp. gr. 1·288, and zinc deposited by a current from two Daniell cells for 30 seconds. The amalgam thus produced would contain 0·0000656 gram of zinc to 100 grams of mercury. The E.M.F. of freshly-prepared amalgam | $ZnSO_4$ |, amalgamated zinc, was then measured and found to be 0·14 volt. After remaining for three hours, the E.M.F had risen to 1·1291 volts, and a further electrolysis for 26 seconds was necessary to restore it to its original value. The above change is, however, only exhibited by an amalgam which contains very small quantities of zinc, and by increasing the quantity of zinc to a sufficient degree the property of the amalgam becomes practically constant.

The suggestion is made that dropping electrodes, similar to those described by the author (*Ann. Phys. Chem.* [2], **41**, 62), might be used in determining the contact difference of potential of metals, if filled with the molten metals, and these be then allowed to flow into some suitable liquid electrolyte. If, as in the case of mercury, there is no potential difference at the place where the metal enters the electrolyte, the potential difference between two such electrodes will be that of the metals which they contain. Great practical difficulties lie in the way of such experiments as those here suggested, but it may in some cases be possible to use in place of the metals themselves the amalgams which they form with mercury. The author describes a number of experiments made in this manner with zinc amalgam, and shows that the E.M.F. amalgam | mercury, varies with the amount of zinc contained in the amalgam, the variation in these experiments being from 0·021 to 0·156 volt. H. C.

Electrical Conductivity of Precipitated Membranes. By G. Tammann (*Zeit. physikal. Chem.*, **6**, 237—240).—A solution of cupric sulphate superposed on a solution of potassium ferrocyanide precipitates at the dividing surface an exceedingly fine membrane of cupric ferrocyanide, which permits the transfusion of water, but not of any of the salts present in the solutions. Notwithstanding this, the author finds that the presence of such a membrane in an electric circuit does not increase the resistance. His mode of experiment was as follows. He prepared solutions of the above-mentioned salts, having equal electrical conductivity, and superposed them in an electrolytic cell, so that one horizontal electrode was in one solution, the other electrode in the other. The current had thus to traverse the precipitated semipermeable membrane, and it was found that the resistance remained exactly as before. A membrane of zinc ferrocyanide behaves similarly at first, but after some time it increases in thickness, becomes opaque and permeable for the salts, its resistance meanwhile growing greater, and attaining a maximum in about 15 minutes. Precipitated membranes of zinc and cupric hydroxides thicken rapidly and diminish the conductivity by from 5 to 8 per cent. Membranes of insulating material, such as pyroxylin, increase the resistance enormously, the only conduction being probably that through the pores. (Compare Ostwald, Abstr., 1890, 1354.) J. W.

Influence of Water of Crystallisation on the Electrical Conductivity of Salt Solutions. By J. TRÖTSCH (*Ann. Phys. Chem.* [2], **41**, 259—287).—The conductivities of solutions of a large number of different salts have been determined for temperatures ranging from 10° to 80°. The Kohlrausch telephone method was employed, and in order to obviate the difficulty arising from evaporation of the solutions at the higher temperatures the top of each solution was covered with a layer of molten paraffin. The conductivities were measured at every 10°, and the difference d between consecutive readings is taken as a mean temperature coefficient for the 10° rise of temperature.

Solutions of salts which are ordinarily anhydrous in the solid state, such as KCl, $NaCl$, KNO_3, have temperature coefficients which rise continually with the temperature, or which attain a maximum and then remain constant. On the other hand, the temperature coefficient of solutions of hydrated salts at first increases, reaches a maximum, and then decreases, the author attributing this last behaviour to the loss by the salt of its water of crystallisation. Calcium chloride forms an exception to this rule, the three solutions examined, which contained 4·5, 19·2, and 32 per cent. $CaCl_2$, behaving throughout as solutions of anhydrous salts. The temperature coefficient in the case of the second solution, however, only undergoes a slight increase with rising temperature, and is far smaller than that of the first or third solutions. Five solutions of cupric chloride were examined, having the percentages 1·35, 9, 18·2, 28·7, 35·2. The two concentrated solutions are green, the two dilute solutions blue, and the colour of the third solution is intermediate between the two. All these solutions behave as solutions of hydrated salts, the temperature coefficient in each case reaching a maximum at between 40° and 50°. At the same temperatures, a change in colour is also observed, the green solutions becoming yellow and the blue solutions becoming green. In each case these changes seem, therefore, to be conditioned by a dehydration of the salt taking place as the temperature rises. Cobalt chloride shows a somewhat similar behaviour, the colour of the solutions changing from red to blue on heating, and at the same time the temperature coefficient reaching a maximum. The temperature of the change is, however, higher in this case, and therefore it is not so readily observed.

The author concludes that salts are contained in solution partly as hydrates and partly in the anhydrous state. At high temperatures, the hydrates part with their water, this taking place the more readily in the more concentrated solutions. The water of hydration exercises a specific influence on the electrical conductivity of solutions.

H. C.

Electrical Conductivity of Saline Solutions. By P. CHROUSHTCHOFF and W. PASHKOFF (*J. Russ. Chem. Soc.*, **22**, 110—115), and by CHROUSHTCHOFF (*ibid.*, 115—116).—The two papers contain a large number of experimental data as regards the conductivity of aqueous solutions of salts and mixtures of salts and acids, but the conclusions arrived at are the same as those contained in Chroushtchoff's previous papers (Abstr., 1889, 808—809). B. B.

Solubility of Mixtures of Electrolytically Dissociated Substances. By A. A. NOYES (*Zeit. physikal. Chem.*, **6**, 241—267).—It has been shown by Nernst (this vol., p. 3) that the principles regulating the influence of two salts on each other's solubility are those deduced from the general law of mass action as interpreted in the light of the electrolytic dissociation theory. The author, in the present paper, contributes an account of his experimental work on the subject. He investigated 11 pairs of salts, and finds the results of his experiments in very good agreement with the theoretical values. Most of the work was done with binary electrolytes, for example, $AgBrO_3 : AgNO_3$, $TlSCN : TlNO_3$, but a few ternary electrolytes were shown to give results equally in harmony with the theory. Experiments were made not only with pairs of salts containing one ion in common, but also with pairs whose ions were all different.

Reckoning back from the solubilities, it is possible to calculate the dissociation constants of strong electrolytes. This is a fact of considerable importance, for the ordinary method of calculation from the electrical conductivity fails in such cases to give a constant number at all. J. W.

Method of Determining Thermal Expansion for Equal Quantities of Heat. By E. J. DRAGOUMIS (*Zeit. physikal. Chem.*, **6**, 281—284).—Let V be the volume of a substance; g its weight; α its coefficient of cubical expansion; c its specific heat; g its specific gravity; Δt the rise of temperature, and A the expansion caused by the communication of 1 cal.; then $A = V\alpha\Delta t$. But $\Delta t = 1/cg$ and $V/g = 1/s$; therefore $A = \alpha/cs$. In the case of gases, A is evidently inversely proportional to the molecular heat, for α is constant for all gases, and s varies inversely as the molecular weight.

The author determines A in the following manner: A dilatometer packed in cotton wool contains the substance whose expansion is to be measured, and also a platinum spiral, the ends of which are fused through the walls. By means of this spiral the substance is heated, a current of about 0·2 ampère being passed. From the current, the heat communicated is easily calculated, and the expansion for this amount is observed. Comparative experiments with various liquids were executed, and the results found to be satisfactory. J. W.

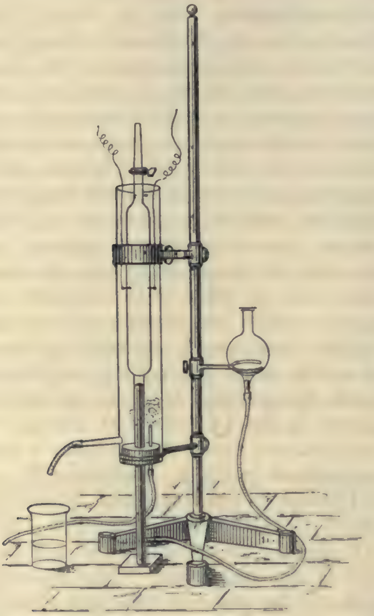
Estimation of the Specific Gravity of Frothy Syrups. By A. GENIESER (*Zeit. ang. Chem.*, 1890, 44—45).—A tared pyknometer is about two-thirds filled with the syrup, in which air-bubbles are entangled, and the weight is noted. It is then carefully heated in a salt bath, and maintained in ebullition for a few moments. The whole of the air rises to the surface, where it forms an extremely thin layer of froth. After cooling, water is added, so as to float on the surface without mixing. The froth readily dissolves, and the air escapes. The pyknometer is then filled to the mark with water, and weighed. On deducting the excess of weight, above that of the syrup taken, from the total amount of water which the pyknometer will contain, the remainder gives the weight of water equal in volume to the syrup taken, and thence the specific gravity. M. J. S.

Dissociation Phenomena. By A. W. v. HOFMANN (*Ber.*, **23**, 3303—3319).—*Dissociation of Carbonic Anhydride.*—In 1860, the author published a paper in conjunction with H. Buff, in which it was stated that carbonic anhydride is gradually decomposed by the passage of a series of electric sparks through the gas, and that after a time the carbonic oxide and oxygen recombine with explosive violence. A repetition of these experiments has shown that the explosion only occurs under certain special conditions. 6—10 c.c. of dry carbonic anhydride under a pressure of 650—700 mm. are brought into a stout glass tube standing over mercury; a short piece of platinum wire is fused into the shorter limb of a thin U-shaped tube, the tube is filled with mercury, and a second piece of wire wound spirally round the outside of the shorter limb, which is then passed up into the vessel containing the gas; in this way the length of the spark may be readily regulated; in general it should be 2·5—3 mm. Connection is made by two wires dipping into the mercury contained in the U-tube and trough respectively. The electric current is obtained from two Bunsen's elements of medium size, which are connected with a Ruhmkorff's coil and a small Leyden jar, the coil being 30 cm. long and 10 cm. in diameter.

The first explosion usually occurs after 15—20 minutes, and the subsequent ones at shorter intervals, since the regeneration of the carbonic anhydride is not complete. The dissociation of carbonic anhydride may be shown by passing the gas through a glass tube, in the middle of which two platinum terminals are fused; a series of sparks is allowed to pass, and the issuing gas collected over potash; part of the gas remains undissolved, and is found to be explosive. Carbonic anhydride does not appear to be at all affected by a glowing spiral of wire; it was not found possible to prepare the gas free from air.

Dissociation of Steam.—The accompanying illustration (next page) shows a form of apparatus which may be employed for the purpose of showing the dissociation of steam at varying pressures. The wide glass tube is 2·5 cm. in diameter and 20 cm. in length, the lower tube is 1 cm. in diameter and 40 cm. in length; the apparatus is filled with moist mercury and heated with steam; instead of fixed terminals, the U-tube and wires described above may be employed; in one experiment 2·9 c.c. of gas were obtained after ten minutes; no regeneration of water occurred, as in the case of carbonic anhydride. The experiment may be varied by allowing the apparatus to cool whilst the electric current is continued; the dissociated gases gradually combine, and the whole tube becomes refilled with mercury. The current employed is obtained from three Bunsen cells, with the coil and Leyden jar as before. Steam may also be dissociated by means of a glowing white hot spiral of platinum wire; the two ends are connected with accumulators, steam is passed over the coil, and the mixed gases are collected over cold water, which serves to condense the excess of steam.

Dissociation of Gases and Vapours by the Silent Discharge.—Experiments in this direction show that ozone is produced by the decomposition of carbonic anhydride, the results of Andrews and Tait, Brodie, and others being thus confirmed. Steam may also be decomposed by passing it through a Siemens ozone tube, or by the use of the modified apparatus devised by Berthelot; various experiments were made to prove that the explosive gas obtained was really derived from the steam, and was not due to electrolysis. Berthelot's results on the decomposition of ammonia by means of the silent discharge are confirmed. The vapours of methyl alcohol, ethyl alcohol, and ethyl ether may also be dissociated by means of the silent discharge.



J. B. T.

Influence of Mineral Acids on the Velocity of the Reaction between Bromic and Hydriodic Acids. By G. Magnanini (*Gazzetta*, **20**, 377—393).—The reaction between bromic and hydriodic acids was shown by Ostwald (Abstr., 1888, 1024) to form an exception to the ordinary rule of mass action, and neither Meyerhoffer's (Abstr., 1889, 9) nor Burchard's (Abstr., 1889, 208) expressions are found to satisfy the experimental data respecting the variation of the speed of the reaction. These discrepancies are evidently occasioned by secondary reactions, which alter the velocity of the changes at every instant. Ostwald found that mineral acids increase the speed of the reaction, and that the increments are sensibly proportional to the affinity coefficients of the respective acids, or to the quantity of hydrogen electrolytically dissociated from them. The author has continued Ostwald's investigations on the accelerating or retarding effects of mineral acids on this reaction, experimenting with hydrochloric, nitric, sulphuric, and bromic acids, with mixtures of some of these acids, and with potassium bromate; from the tabulated results, he draws the following conclusions. During the course of the different changes, the reaction is influenced in the same way by the secondary actions. The reciprocal values of the times required for the separation of a determinate quantity of iodine vary as the velocity of the respective reactions. The velocity of the reaction is accelerated by hydrochloric acid, but the acceleration is not proportional to the quantity of acid present. The quantity of iodine deposited after equal times in presence of equivalent quantities of hydrochloric and nitric acids is the same. Mixtures of hydrochloric and nitric acids, in any proportions, are equivalent to either of the acids, so that, independently of the nature of the electro-negative radicle, it may be said that the velocity of the reaction depends entirely on the quantity of hydrogen electrolytically dissociated, without, however, being proportional to it. The action of sulphuric acid is more complicated, on account of the incomplete dissociation of that acid. The accelerating effect of bromic acid is almost six times that of hydrochloric or nitric acid. S. B. A. A.

Velocity of the Halogenisation of Fatty Hydrocarbons. By M. Wildermann (*Ber.*, **23**, 3174—3175).—The following two laws are deduced from a study of the action of bromine or chlorine in sunlight on amyl bromide, amylene bromide, liquid and solid tribromopentane, tetrabromopentane, and amylene chloride:—(1) Substitution proceeds more slowly as the quantity of positive hydrocarbon becomes smaller. (2) The larger the quantity of hydrocarbon present, the quicker the substitution. J. B. T.

Cryoscopic Investigation of Colloïdal Substances. By A. Sabanéeff (*J. Russ. Chem. Soc.*, **22**, 102—107).—The author has shown that Raoult's method may be conveniently employed for the determination of the molecular weight of colloïdal substances (Abstr., 1890, 1215). Similar results were obtained by Morris and Brown, by Ekstrand and Mauzelius. On the other hand, Paternò, in his research on gallic and tannic acids, has arrived at the conclusion that their molecular weights cannot be determined by Raoult's method. The values obtained by Paternò give 10 mols. of the first, and 109 mols. of the second, as the molecular weights in solution. The author shows that Paternò's paper includes an error in calculation, and that the values greatly depend on the purity of the material. First the molecular weight of gallic acid was determined. It was dried at 120°, losing 9·65 per cent. water, corresponding with the formula $C_7H_6O_5 + H_2O$. In aqueous solution, containing 0·5238 per cent., the depression was 0·06°, and the molecular weight 166; in acetic acid, containing 0·4107 part, the depression was 0·095°, molecular weight = 168, whereas the value for $C_7H_6O_5$ is 170; gallic acid exists, therefore, as a single molecule in solutions.

Commercial tannin was found to contain some gallic acid, the quantity of which, as calculated from the depression of the impure preparation, compared with that of the pure preparation, was found to be 2·39 per cent. It was dried for 20 hours at 120°, and the loss was 10·66 per cent. Aqueous solutions with a concentration of 0·822—3·773 show a depression of 0·015—0·060, giving a molecular weight of 1044—1195 (mean, 1104). More concentrated solutions, containing 5·5 to 9·5 per cent., gave higher molecular weights, 1497 to 2436, but the values are useless, as solutions of more than 4 per cent. of tannin in water become turbid at 0°, tannin separating out. In Paternò's solutions, containing 11·5—23 per cent. of tannin, $\frac{1}{2}$—$\frac{2}{3}$ of the tannin must have separated at 0° in the insoluble state, and his (corrected) molecular weights, = 2643—3700, are of no value. The author finds in acetic solution, molecular weights = 1105—1114 (mean 1113). Pure tannin was prepared by Löwe's method, but it was impossible to work with aqueous solutions, as not more than 0·5 per cent. is dissolved in water at 0°, and even such weak solutions became turbid. In acetic acid solution, as a mean, M = 1322 was found, whereas, M calculated for $(C_{14}H_{10}O_9)_4 = 1288$, so that tannin exists in solutions as a quadruple molecule. The author thinks that Paternò's tannin was not quite dry, and shows by experiment that such a preparation causes a much larger depression, owing to the contamination of the glacial acetic acid by the water of crystallisation of the compound. The author says that the empirical formula of tannin requires confirmation by further research. B. B.

Apparatus for Distillation under Reduced Pressure. By H. Wislicenus (*Ber.*, **23**, 3292—3295).—The author describes two forms of apparatus for use with the the Bunsen pump, to prevent backward diffusion. The first consists of a tube, with one round and one pear-shaped bulb; in the depression between these a rubber ring is placed, one end of the tube is sealed, a small opening is made in the side and is covered with a piece of rubber tube, or an ordinary Bunsen valve may be attached; the other end of the tube is connected with the vessel to be exhausted, the pear-shaped bulb fits into a wide tube, the rubber ring serving to make the connection air-tight; the second tube is joined to the pump in the usual manner. The second form of valve consists of two tubes, one closely resembling a thistle funnel, the narrow end of which is attached to the pump; a bulb with a small aperture is blown at the end of the second tube, and it is covered with a rubber cap, through which an opening is pierced at a little distance from the one in the glass; the rubber cap serves to make an air-tight connection between the bulb and the wide end of the first tube.

An apparatus for fractional distillation under reduced pressure is also described; it consists of a combination of several of the first of these joints, and provision is made for changing the receiver without interrupting the distillation. J. B. T.

Isomorphism. Part III. By J. W. Retgers (*Zeit. physikal. Chem.*, **6**, 193—236).—In this communication (for previous papers see Abstr., 1890, 328, 1208), the author first discusses the relations of morphotropy. He would limit the term morphotropic to such substances as show a total analogy of form, and not, for instance, merely analogy of angles in one zone. Isomorphous substances have not only this total form-analogy, but also analogy of chemical constitution. Morphotropic substances are not necessarily chemically analogous, but must be chemically connected with each other. Substances which show a total form-analogy, but have no chemical resemblance, are termed isogonic. In the regular system, for instance, potassium chloride and rubidium chloride are isomorphous; potassium chloride and sodium chloride, morphotropic; and sodium chloride and sodium chlorate, isogonic.

Isomorphous mixtures are proved by the continuous linear change of physical properties with the composition of the mixture. No intimate crystalline mixture can be obtained with merely morphotropic substances, and in this case identity of system, and of degree of hemihedry, are not essential. The author rejects Marignac and Klein's conception of mass isomorphism, according to which an element or group, largely preponderating in a compound, determines the crystalline form, no matter what the other components may be. It is the *volume* and not the *weight* of the group that is decisive.

An investigation follows of the supposed isomorphism between potassium and sodium sulphates. The author proves that a definite double salt, $3K_2SO_4,Na_2SO_4$, crystallises from a solution of the mixed sulphates. It usually crystallises in hexagonal prisms or pyramids, but when the mother liquor contains sodium chloride, it separates in tables—the "plate-sulphate" obtained in the manufacture of iodine from kelp. Potassium chloride does not effect this change of form. The three simple forms are then—

K_2SO_4. Rhombic, pseudo-hexagonal. Forms pyramids and prisms of hexagonal section. Optically biaxial. Weak birefringence. Sp. gr. = 2·666. Not easily fusible.

$3K_2SO_4,Na_2SO_4$. Hexagonal. Forms pyramids and prisms. Optically uniaxial. Marked birefringence. Sp. gr. = 2·695. Easily fusible.

Na_2SO_4. Rhombic, but not pseudo-hexagonal. Forms only pyramids with rhombic section. Optically biaxial. Strong birefringence. Sp. gr. 2·673. Fusible with great difficulty.

The double salt is not an isomorphous mixture, as is shown by a consideration of its properties in relation to those of the simple salts. Each simple salt can take up a minute quantity of the other, which points to a very limited isodimorphism. The general results are—

(1) K_2SO_4 and Na_2SO_4 are not isomorphous.

(2) They only form one double salt, $3K_2SO_4,Na_2SO_4$.

(3) From mixed solution the pure double salt separates out alongside one or other of the simple salts.

(4) K_2SO_4 and the double salt are morphotropic.

(5) Na_2SO_4 is not morphotropic either with K_2SO_4 or with the double salt, but is crystallographically completely independent.

The dolomite series is next discussed. In this series we have calcspars containing a little magnesium carbonate, magnesites containing a little calcium carbonate, and dolomites which have the two salts in nearly equal molecular proportions. Calculated from the specific gravities of the component salts, that of dolomite should be 2·843; it is actually 2·872. The author considers the series not isomorphous, but merely morphotropic. J. W.

Inorganic Chemistry.

Affinities of Iodine in Solution. By H. GAUTIER and G. CHARPY (*Compt. rend.*, **111**, 645—647).—If mercury is agitated with any solution of iodine, a green precipitate of mercurous iodide is formed, but if the mercury contains another metal, the iodine combines with the latter in proportions depending on the nature of the solvent. In the case of an amalgam of lead, the difference in colour between lead and mercurous iodides enables the change to be followed.

Brown solutions of iodine (in alcohol, ether, acetone) yield with lead amalgam a yellow precipitate of lead iodide, even when the proportion of lead is very small, and no mercurous iodide is formed until all the lead has been converted into iodide.

On the other hand, violet solutions of iodine (in chloroform, carbon bisulphide) give green mercurous iodide, even in presence of considerable quantities of lead and when the iodine is in excess.

Solutions of intermediate tint give precipitates intermediate in colour between lead iodide and mercurous iodide, and it is found that if the solutions of iodine in various solvents are arranged in order according to their colour, and also according to the colour of the precipitate which they yield when agitated with lead amalgam, the two orders are the same. The colour of the precipitate is independent of the composition of the amalgam and the concentration of the iodine solution.

Careful examination of the reaction shows that brown solutions of iodine and pure mercury at first yield mercuric iodide, which passes into solution, whilst violet solutions of iodine at once form mercurous iodide, even whilst some free iodine remains. In presence of lead amalgam, brown solutions of iodine first form mercuric iodide, which attacks the lead, forming lead iodide and mercurous iodide, and the latter is again converted into mercuric iodide by the free iodine. No permanent precipitate of mercurous iodide is formed with brown solutions until all the lead has been converted into iodide.

It follows from these results that violet solutions of iodine contain the element in a more simple molecular condition, with a tendency to at once form mercurous iodide, this tendency being more marked, the simpler the condition of the iodine. The phenomena seem to belong to the same order as those to which Berthelot has given the name "tendency to conservation of type." C. H. B.

Fluorspar from Quinciė. By H. BECQUEREL and H. MOISSAN (*Compt. rend.*, **111**, 669—672).—It is well known that certain specimens of fluorspar, when powdered, emit a peculiar odour, which has been attributed by different observers to free fluorine, hypochlorous acid, ozone, hydrocarbons, &c. The fluorspar examined by the authors was deep violet in colour, and came from Quincié, near Villefranche. It had the composition Ca, 36·14 (= CaF_2, 70·47); $Fe_2O_3 + Al_2O_3$, 3·95; SiO_4, 25·00; loss at a red heat 2·10 per cent; sp. gr. 3·117.

When powdered, it emitted an odour recalling that of ozone and likewise that of fluorine. Moissan has shown that fluorine decomposes water with liberation of ozone. The odour from the fluorspar is very similar to that emitted from the electrolytic cell in the isolation of fluorine, and even if the odour is due to ozone, the latter may be a product of the action of free fluorine on the moisture of the air.

Fluorspar from Quincié, when powdered in contact with moist air, evolves a gas which at once acts on ozone paper. If moistened with starch paste and potassium iodide solution, and powdered under a microscope, bubbles of gas are seen to escape, and an intense blue coloration is produced. When the fluorspar is powdered with sodium chloride or potassium bromide or iodide, free chlorine, bromine, or iodine is liberated. When heated above a red heat, the fluorspar decrepitates, loses its colour, and becomes ochreous, and afterwards gives no trace of ozone when powdered. If heated at 250° for an hour, which is quite sufficient to destroy all ozone, it still gives, when powdered, a strong reaction with ozone paper.

Small fragments of the mineral, when heated in a small glass tube, corrode its surface; when powdered with silicon, a pungent odour is emitted, and if the mixture is heated, silicon fluoride is evolved. If small fragments of the mineral are left in contact with water, the water becomes acid, and if the liquid is then evaporated in watch glasses, the latter are corroded.

No similar results were obtained with a white fluorspar from the Pyrenees, and although it is possible that the fluorine results from the dissociation of a perfluoride, the authors regard it as more probable that the free fluorine is occluded in the mineral.

C. H. B.

The Molecular Weight and Refractive Energy of Sulphur Dichloride. By T. Costa (*Gazzetta*, **20**, 367—372).—The existence of a definite compound of the composition SCl_2 has been repeatedly called in question (see this Journal, 1870, 455; 1871, 1163; Abstr., 1878, 553; 1886, 977); and the substance held by some to be sulphur dichloride has been variously regarded as a solution of chlorine in the monochloride, or as a compound in a state of partial dissociation. The author has determined cryoscopically the molecular weight of the reddish-brown liquid obtained by saturating the monochloride with chlorine below 0°, and then removing any excess of chlorine by passing in a current of carbonic anhydride, and the results of the determinations, both in benzene and acetic acid solution, agree with the molecular formula SCl_2. This substance can, therefore, no longer be said to exist in a state of partial dissociation. Its density at 15·4° is 1·64819 and its molecular refractive energy $\mu_{H\alpha} = 1·57169$, $\mu_{Na} = 1·57806$.

S. B. A. A.

Specific Gravity of Sulphuric Acid of Different Degrees of Concentration. By G. Lunge and M. Isler (*Zeit. ang. Chem.*, 1890, 129—136).—In consequence of the discovery of errors in Kolb's table, the authors have made fresh determinations with great care. The curve plotted from the results, whilst agreeing in many places closely with that of Kolb, is much smoother, and at the extremes, differs somewhat considerably. The table, of which the following is an abstract, was obtained by graphic interpolation; in the original, it is given for intervals of 0·005 (1° Twaddell) in the specific gravity:—

Sp. gr. at $\frac{15^\circ}{4^\circ}$ *in vacuo.*	Percentage of H_2SO_4.	Sp. gr. at $\frac{15^\circ}{4^\circ}$ *in vacuo.*	Percentage of H_2SO_4.	Sp. gr. at $\frac{15^\circ}{4^\circ}$ *in vacuo.*	Percentage of H_2SO_4.
1·000	0·09	1·400	50·11	1·800	86·90
1·020	3·03	1·420	52·15	1·820	90·05
1·040	5·96	1·440	54·07	1·824	90·80
1·060	8·77	1·460	55·97	1·826	91·25
1·080	11·60	1·480	57·83	1·828	91·70
1·100	14·35	1·500	59·70	1·830	92·10
1·120	17·01	1·520	61·59	1·832	92·52
1·140	19·61	1·540	63·43	1·834	93·05
1·160	22·19	1·560	65·08	1·836	93·80
1·180	24·76	1·580	66·71	1·838	94·60
1·200	27·32	1·600	68·51	1·840	95·60
1·220	29·84	1·620	70·32	1·8405	95·95
1·240	32·28	1·640	71·99	1·8410	97·00
1·260	34·57	1·660	73·64	1·8415	97·70
1·280	36·87	1·680	75·42	1·8410	98·20
1·300	39·19	1·700	77·17	1·8405	98·70
1·320	41·50	1·720	78·92	1·8400	99·20
1·340	43·74	1·740	80·68	1·8395	99·45
1·360	45·88	1·760	82·44	1·8390	99·70
1·380	48·00	1 780	84·50	1·8385	99·95

M. J. S.

Reduction of Oxygen Compounds with Sodium. By M. Rosenfeld (*Ber.*, **23**, 3147—3149).—Sodium may be obtained in a finely-powdered condition by trituration with some other solid substance. Such a mixture of sodium and zinc oxide ignites spontaneously, and leaves a residue of metallic zinc. Ferric oxide and lead oxide react in a similar manner, whilst gypsum is reduced to calcium sulphide. Certain organic compounds, such as pyrogallol, wheat starch, or salicylic acid, inflame immediately on admixture with sodium, carbon being separated; other substances, such as milk sugar and cane sugar, after admixture with sodium, require to be exposed to moist air before reaction takes place. In the case of compounds which only contain carboxylic oxygen, the sodium salt of the acid is formed. Sodium benzoate and sodium oxalate are obtained from benzoic and oxalic acids respectively. The carbonaceous residue from rosaniline, toluidine, albumin, and other amido-compounds contains sodium cyanide; brucine, morphine, and strychnine yield a porous mass of charcoal free from cyanogen. Both sodium cyanide and sodium cyanate were obtained from uric acid. "Saccharin" yields a residue containing sodium thiosulphate and sodium cyanide.

J. B. T.

Ammonium Pyrosulphite. By A. FOCK and K. KLÜSS (*Ber.*, **23**, 3149—3151).—Ammonium pyrosulphite, $(NH_4)_2S_2O_5$, is prepared by passing sulphurous anhydride into cold, concentrated, aqueous ammonia until the liquid becomes yellow; it is then allowed to evaporate spontaneously in a vacuum. The salt crystallises in large, thick, deliquescent plates, which belong to the rhombic system. Marignac has shown that the corresponding potassium salt crystallises in the monoclinic system.

J. B. T.

Properties of some Beryllium Salts and of the corresponding Aluminium Compounds. By F. SESTINI (*Gazzetta*, **20**, 313—319).—(1.) *Phosphates.* The phosphates were prepared in the gelatinous state by precipitating beryllium sulphate and potassium alum respectively with disodium phosphate, and washing the precipitate for 4 to 6 days; they are both sparingly soluble in distilled water, the beryllium salt being considerably the more soluble of the two. On igniting the moist beryllium phosphate, it left 6 per cent. of its weight of white anhydrous phosphate. A litre of a saturated solution of beryllium phosphate in 2 per cent. acetic acid contains 0·550 gram of the anhydrous salt (containing, however, 74·9 per cent. P_2O_5 instead of 74·2 per cent.). A similar solution of the aluminium salt, however, contains 0·375 gram of phosphate dissolved, containing 87·1 per cent. P_2O_5 (instead of 54·8 per cent.); this excess of acid is probably due to the formation of a little beryllium pyrophosphate and to the conversion of a portion of the aluminium phosphate by the acetic acid into a more soluble acid phosphate.

A litre of a saturated solution of the beryllium salt in 10 per cent. acetic acid contains 1·725 grams, and the corresponding aluminium solution 0·30 gram of the respective anhydrous phosphates. On gently heating the acetic acid solution of beryllium phosphate, it becomes turbid, and near the boiling point a white precipitate of a basic phosphate, of the formula $3BeO,P_2O_5,3H_2O + Aq$, is deposited; a solution of the aluminium salt at most becomes opalescent.

(2.) *Carbonates.*—100 c.c. of water saturated with carbonic anhydride at the ordinary pressure dissolves 0·185 gram of anhydrous beryllium oxide, and the solution becomes turbid on agitation or on boiling. Under the same conditions, only 0·001 gram of aluminium oxide passes into solution. The solubility of the beryllium oxide is due, according to the author, to the formation of an acid carbonate.

S. B. A. A.

Magnesium Lead Chloride. By R. OTTO and D. DREWES (*Arch. Pharm.*, **228**, 495—498).—A hot concentrated magnesium chloride solution dissolves a considerable amount of lead chloride and deposits, on cooling, a double chloride, $PbCl_2,2MgCl_2 + 13H_2O$, in small, white, lustrous, indistinct crystals. The salt is exceedingly hygroscopic; moisture quickly converts it into a solution of magnesium chloride, holding lead chloride in suspension. Calcium and lead chlorides appear to give a similar compound. J. T.

Electrolysis of Fused Aluminium Fluoride. By A. Minet (*Compt. rend.*, **111**, 603—606). The composition of the bath which gives the best results corresponds with the formula $12NaCl + Al_2F_6,6NaF$; melting point 675°; temperature at which vapours are evolved, 1035°; sp. gr. at 820° = 1·76; coefficient of expansion 5×10^{-4}; electrical conductivity at 870° = 3·1. The relation of the conductivity to the temperature is expressed by the equation $C_t = 3{\cdot}1[1 + 0{\cdot}0022(t - 870^\circ)]$. For a current of 1200 ampères, the mass of the bath is 20 kilos., the intensity of the current at the positive pole is 1 ampère, and the difference of potential between the electrodes is 5·5 volts. The composition of the bath is kept constant by the gradual addition of a mixture of aluminium hydroxide, $Al_2O_2(OH)_2$, 416·4 parts, cryolite, 210·4 parts, and aluminium oxyfluoride, $Al_2F_6,3Al_2O_3$, 238·4 parts.

The difference of potential, ϵ, between the electrodes when the electromotive force is considerably below that required to produce decomposition is expressed by the equation $\epsilon = KI$, I being the intensity of the current, and the temperature being constant. As the point is approached at which the electromotive force of polarisation is equal to the electromotive force of decomposition of the electrolyte, the difference of potential cannot be calculated by means of any simple expression. At 870°, the maximum density of the current at the electrodes, corresponding with the first period of electrolysis of the bath specified, varies between 0·02 and 0·03 ampère.

During the second period of electrolysis, when the electromotive force is sufficient to produce decomposition, up to a density of 1 ampère at the positive electrode, the difference of potential is expressed by the equation $\epsilon = e + \rho I$, where e is the electromotive force of decomposition, and ρ is the resistance of the electrolyte. At 852°, $e = 2{\cdot}15$ and $\rho = 0{\cdot}01$; at 890°, $e = 2{\cdot}40$ and $\rho = 0{\cdot}0044$; at 980°, $e = 0{\cdot}34$ and $\rho = 0{\cdot}0033$. For densities of current higher than 1 ampère, the difference of potential cannot be calculated as a function of the intensity of the current by any simple expression; it rapidly attains a value similar to that existing in the electric arc.

In presence of salts of iron or silicon, within certain limits of density of current at the positive electrode, the salts decompose according to Sprague's law. At 810°, with salts of iron, $e = 0{\cdot}75$ and $\rho = 0{\cdot}0093$; at 840°, with silicon compounds, $e = 1{\cdot}37$ and $\rho = 0{\cdot}0089$; at 870°, with aluminium salts, $e = 2{\cdot}15$ and $\rho = 0{\cdot}0085$.

C. H. B

Preparation of Chromium from Potassium Chromium Chloride and Magnesium. By E. Glatzel (*Ber.*, **23**, 3127—3130).—Chromium can be quickly prepared in an almost chemically pure condition in the following manner:—Potassium dichromate (100 grams) is dissolved in the least possible quantity of water, the solution mixed with hydrochloric acid of sp. gr. 1·124 (400 c.c.), and then 80 per cent. alcohol (100 c.c.) gradually added. The solution of potassium chromium chloride obtained in this way is treated with potassium chloride (160 grams), the filtered solution evaporated to dryness, the residue heated until anhydrous, freed from the green portions, which are produced by the decomposition of the double salt, then powdered, and mixed with magnesium filings (50 grams). This mixture is heated, for about half an hour, to a bright-red heat, in a closed Hessian crucible in a wind-furnace, care being taken that the potassium chloride does not volatilise completely, otherwise the chromium is partially oxidised. The melt is separated from the superficial layer of chromium oxide, treated with water, and the finely divided metal freed from salts and unchanged magnesium by washing it with water, then boiling it with dilute nitric acid, and again washing with water, all the washing being done by decantation. The yield of the metal, dried at 100°, is about 27 grams.

Chromium, prepared in this way, is a light-grey, crystalline, non-magnetic powder of sp. gr. 6·7284 at 16°; it can be melted in a Deville's furnace, but only with great difficulty, and after being melted it shows a silvery fracture. Two analyses of the powder showed that it contained 99·53 to 99·57 per cent. of chromium, and that it was free from silver and magnesium. F. S. K.

Mineralogical Chemistry.

Selenium and Tellurium Minerals from Honduras. By E. S. DANA and H. L. WELLS (*Amer. J. Sci.*, **40**, 78—82).—The authors received a number of specimens of minerals containing selenium and tellurium from El Plomo mine, Ojojama District, Honduras. Two of these have proved to be of unusual interest. The first occurs in massive forms, with hexagonal cleavage, of a blackish-grey colour, disseminated through a gangue consisting chiefly of quartz and barytes. After deducting 65·68 per cent. of gangue, the analytical results obtained were as follows:—

Se.	Te.	Total.
29·31	70·69	100·00

The mineral is obviously an isomorphous mixture of selenium and tellurium, and is of great interest in that it is the nearest approach to native selenium which has yet been found. The authors propose to call this mineral *Selen-tellurium*. In connection with the hexagonal cleavage of this mineral, it is interesting to note the recent observations of Muthmann (*Zeit. f. Kryst.*, **17**, 356), showing the existence of an allotropic form of metallic selenium in hexagonal-rhombohedral crystals, closely isomorphous with tellurium. In the analysis, the separation of selenium and tellurium was effected by the method of Divers and Shimosé (Trans., 1885, 439).

The second mineral is obviously an oxidation product of a greenish-yellow colour. Analysis shows it to be a normal ferric tellurite of the composition $Fe_2O_3,3TeO_2 + 4H_2O$. That the mineral is a ferric tellurite is evident since it gives off no chlorine when boiled in hydrochloric acid, nor does it give any reaction for ferrous iron when dissolved in cold hydrochloric acid. Two other tellurium-iron minerals have been described, namely, Genth's *ferrotellurite* and Hillebrand's *emmonsite* (Abstr., 1887, 344). The former is a ferrous tellurite widely different in appearance from the Honduras mineral, for which the authors, therefore, propose the name of *Durdenite*, after the gentleman to whom they are indebted for the material used.

In a note appended to the paper, W. F. Hillebrand gives the results of a repetition of the analysis of emmonsite, which upholds the accuracy of his former analysis, and seems to prove that the two minerals are distinct. B. H. B.

Fluorspar from Quincié. By H. BECQUEREL and H. MOISSAN (*Compt. rend.*, **111**, 669—672).—See this vol. p. 148.

New Variety of Zinc Sulphide. By J. D. ROBERTSON (*Amer. J. Sci.*, **40**, 160—161).—A peculiar variety of zinc sulphide has been found in south-eastern Kansas, remarkable from the fact that it is nearly pure white and completely amorphous. It is found in the centre of the town of Galena, Cherokee Co., Kansas. When taken from the mine, it is soft, full of water, and resembles white lead ground in oil. Evidence points to the existence of a large body of this peculiar ore in the mine. An analysis of a dried sample yielded:

Insol. matter.	Zn.	S.	Fe_2O_3.	Total.
2·52	63·70	30·77	2·40	99·39

The water contained in the original sample showed a slight amount of sulphuric acid. This sulphide was evidently formed by the precipitation of zinc sulphate, resulting from the oxidation of blende, by hydrogen sulphide or an alkaline sulphide.

B. H. B.

Contributions to Mineralogy. By F. A. GENTH (*Amer. J. Sci.*, **40**, 114—120).—1. *Tetradymite.*—This mineral occurs, in crystals suggesting an orthorhombic form, near Bradshaw City, Arizona. After subtracting 15·6 per cent. of quartz and 1·8 per cent. of ferric oxide, the analysis gave:

S.	Te.	Bi.	Total.
4·50	33·25	62·23	99·98

These results give a formula analogous to that of bismuthinite.

2. *Iron Pyrites.*—The occurrence of cobalt arsenate with the octahedral crystals of iron pyrites at the French Creek iron mines, Pennsylvania, suggested an analysis of the latter, which gave the following results:—

S.	As.	Cu.	Ni.	Co.	Fe.	Total.
54·08	0·20	0·05	0·18	1·75	44·24	100·50

3. *Quartz, Pseudomorphous after Stibnite.*—Specimens from Durango, Mexico, were found to contain stibnite completely altered into a yellowish-white quartz.

4. *Gold in Turquoise.*—In many collections, specimens of gold enclosed in a bluish-green mineral are represented as turquoise with gold from Los Cerillos, New Mexico. Specimens analysed by the author are proved to contain no turquoise; in one case, the gold-bearing mineral was a chromiferous clay, and in the other, quartz admixed with chrysocolla.

5. *Zircon.*—With the masses of monazite, at Mars Hill, Madison Co., North Carolina, large crystals of zircon, with a sp. gr. of 4·507, occasionally occur. On analysis, the following results were obtained:—

SiO_2.	ZrO_2.	Fe_2O_3.	Loss on ignition.	Total.
31·83	63·42	3·23	1·20	99·68

6. *Scapolite.*—At the Elizabeth mine, French Creek, Pennsylvania, small crystals of scapolite occasionally occur, filling cavities of grey garnet, associated with magnetite, pyrites, and remnants of the essonite from the alteration of which it appears to have been derived. The scapolite is colourless to white; it has a sp. gr. of 2·675, and on analysis gave the following results (I):—

	CO_2.	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.
I.	2·63	52·30	23·68	0·58	0·05	12·36	6·29
II.	1·71	41·42	18·09	10·81	0·59	26·19	—

	K_2O.	Loss by ignition.	MnO.	Total.
I.	0·77	1·50	—	100·16*
II.	—	0·51	0·88	100·20

The second analysis is of the grey garnet which also results from the alteration of essonite.

7. *Titaniferous Garnet.*—A variety of garnet from the Jones mine, Green River, North Carolina, gave, on analysis, the following results:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Loss on ignition.	Total.
35·56	4·58	4·43	20·51	1·88	0·17	31·90	0·55	99·58

8. *Allanite.*—The author analysed two specimens of allanite with the following results:—

	SiO_2.	ThO_2.	TiO_2.	$\underbrace{CeO_2(LaDi)_2O_3}$.		Y_2O_3.	Al_2O_3.	Fe_2O_3.
a.	31·67	0·33	—	23·98		0·36	12·20	4·42
b.	32·04	—	0·12	12·91	10·24	0·33	14·02	7·17

	FeO.	MnO.	MgO.	CaO.	Loss on ignition.	Total.	Sp. gr.
a.	10·89	2·52	2·08	9·37	2·25	100 07	3·546
b.	7·52	0·37	1·47	11·34	2·63	100·16	3·491

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* 100·06 in original.

a. Colour, velvet-black; *b.* Deep brownish-black.

9. *Lettsomite.*—The author has analysed specimens of this rare material from two new localities: the Copper Mountain mine, near Morenci, Arizona, and Copperopolis, Tintic District, Utah. In both cases, the analysis gives results closely agreeing with those demanded by the formula $Cu_4Al_2(OH)_{12}SO_4+2H_2O$. B. H. B.

Synthesis of Rubies. By E. FREMY and A. VERNEUIL (*Compt. rend.*, **111**, 668—669).—The authors have made several important modifications in their process for the manufacture of artificial rubies, and are now able to obtain much larger crystals. The alumina in addition to the small quantity of chromium is made alkaline with potassium carbonate, which facilitates the formation of the crystals but does not enter into their composition. It is advantageous not to mix all the materials but to keep the alumina separate from the fluorides of the alkaline earths, and in this way the mineralisation is effected by the interaction of the gases and vapours. The time of heating is extended to not less than a week; gas furnaces are used in place of coke, and the crucibles have a capacity of several litres, and are capable of producing as much as three kilos. of rubies at each operation.

Natural rubies are found which in parts have the colour of the sapphire. Similar crystals are obtained amongst the artificial products, and there can therefore be little doubt that the colours of the ruby and the sapphire are both due to chromium, probably in different states of oxidation.

The artificial rubies have been used as pivots in watches, and are not inferior to the natural stones in hardness. C. H. B.

Curious Occurrence of Vivianite. By W. L. DUDLEY (*Amer. J. Sci.*, **40**, 120—121).—Two miles above Eddyville, Kentucky, "blue roots" were discovered embedded in a stratum of clay in such position as to indicate that they were in the place of their growth. The blue mineral, which has almost wholly replaced the woody fibre of the roots, is of a deep-blue colour. It is earthy and very friable, and gave, on analysis, the following results:—

Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	P_2O_5.	H_2O at 100°.	H_2O at 230°.	Total.
17·74	9·35	24·58	0·59	0·43	27·71	10·59	7·24	100·07

These results seem to indicate that the ferrous iron in the mineral is combined with the phosphoric anhydride to form vivianite, and if the double mol. of vivianite, $2(Fe_3P_2O_8 + 8H_2O)$, be subtracted, there remains an almost dehydrated double mol. of turquoise, $Al_8P_4O_{22} + 10H_2O$, in which 1 mol. of ferric oxide has replaced one of alumina.
B. H. B.

Dihydrothenardite. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, **22**, 26—27).—Owing to an inexplicable mistake, a new mineral, dihydrothenardite, $Na_2SO_4 + 2H_2O$, was described by the author (Abstr., 1888, 794), whereas a renewed investigation shows that it is astrachanite (hydrated sulphate of sodium and magnesium) containing a considerable quantity of thenardite. B. B.

Connellite from Cornwall. By S. L. PENFIELD (*Amer. J. Sci.*, **40**, 82—86).—Connellite is of special interest to the author, owing to its apparently close relation to the new mineral *spangolite*, recently described by him (Abstr., 1890, 1073). On examining a specimen from Camborne, the author found that the habit of the crystals agrees well with the general description given by Maskelyne in 1863. The analysis, in which the author places great confidence, gave the following results:—

SO_3.	Cl.	CuO.	H_2O.	Loss at 100°.	Total.	Less O.
4·9	7·4	72·3	16·8	0·4	101·8	1·7

The ratio is not very satisfactory, unless it is assumed that some OH is isomorphous with the Cl, in which case the formula may be written $Cu_{15}(Cl,OH)_4SO_{16},15H_2O$. The mineral is very similar to spangolite in composition, both minerals being very basic sulphatochlorides. B. H. B.

Nickel Ores from New Caledonia. By T. MOORE (*Chem. News*, **62**, 180—181).—The ore known as garnierite is found in or near serpentine masses or mountains, either as cementing material in agglomerations of rounded serpentine pebbles or as an interstitial deposit between thin layers of quartz, steatite, and various hydrated magnesium silicates. The associated minerals vary, but comprise quartz, magnesium silicates, and iron oxides; sometimes one predominates, sometimes another, the others being even absent; it is also accompanied at times by chrome-iron ore and surrounded by a ferruginous earth.

The colour of garnierite varies from pale-green in poor ores to warm dark-green in the richer ones, and passes through almost imperceptible shades to light- and chocolate-browns. It crumbles gradually to powder, on exposure to weather, the brown more readily

	Green ores.		Brown ores.			Ferruginous brown ore.
	1.	2.	3.	4.	5.	6.
SiO_2 ...	35·55	36·24	36·25	34·78	35·80	20·57
NiO....	48·38	44·94	46·30	43·79	43·54	15·56
MgO ...	5·02	8·75	–	2·75	2·65	0·81
Fe_2O_3...	1·41	0·21	9·00	6·30	10·73	49·03
Al_2O_3 ..	1·09	1·03	—	—	—	—
Cr_2O_3 ..	0·15	—	0·14	—	—	3·82
MnO ...	—	—	—	—	0·19	trace
H_2O ...	8·85	8·98	9·20	12·40	8·00	10·32
Totals ..	100·45	100·15	99·89	100·02	100·91	100·17

than the green varieties; in all forms it dissolves readily in hot hydrochloric acid, leaving a non-gelatinous silica. In the table (p. 157), are given numbers, corrected for quartz, obtained in the analysis of samples of pure ore; samples previously analysed by other workers appear to have been contaminated with gangue:—

Samples 1 and 2 were a fine, brilliant grass-green; hardness, 2—3; sp. gr. 3; streak, light-green; lustre, waxy and slightly translucent at their edges. Before the blowpipe, the colour becomes dark olive-green, or red in presence of much iron.

3, 4, and 5 were various shades of brown, streak yellow to brownish-yellow, fracture conchoidal with resinous lustre, sp. gr. and hardness the same as green ore, but were rather more brittle. From these numbers, both kinds of ore seem to approach very nearly to a hydrated silicate of the composition $7NiO,6SiO_2,xH_2O$, part of the nickel being replaced by magnesia, iron oxide, or alumina.

The ores represented by sample 6 are light-brown in colour, resembling limonite, are easily marked by the nail, and do not seem to belong to the same class as the others just described.

D. A. L.

Minerals occurring near Port Henry, New York. By J. F. KEMP (*Amer. J. Sci.*, **40**, 62—64).—At the abandoned Pease quarry, a short distance north-west of Port Henry, a face of white, crystalline limestone has been laid bare, and in this occur streaks of hornblende, plagioclase, muscovite, and quartz, but containing as well a great abundance of yellowish-brown titanite crystals; fine brown tourmalines also occur. West of this quarry is another, where flux is being obtained for local furnaces. The rock, a crystalline limestone, contains small, hexagonal tables of graphite disseminated through it. Occasionally lemon-yellow calcite is found, with fine crystals of clear calcite of great crystallographical interest as being good illustrations of oscillatory forms. Further west is the Treadway quarry in ophicalcite, containing streaks of pyrrhotite, phlogopite, brown tourmaline, and well-crystallised light-brown tremolite. The abandoned quarry six miles north-west of Port Henry, the source of the well-known tourmaline crystals, is probably a felspathic mass either in gneiss or in granite, and cut by three narrow dykes of altered diabase. Great masses of biotite and fine specimens of rose-quartz are also met with. The so-called Lover's Pit at Mineville is affording crystals and cleavage masses of magnetite of unusual size and excellence.

B. H. B.

Fayalite in the Obsidian of Lipari. By J. P. IDDINGS and S. L. PENFIELD (*Amer. J. Sci.*, **40**, 75—78).—The Lipari Islands have long been celebrated for their acid lavas and pumices. The chief interest in connection with these rocks attaches itself to the fayalite crystals in the cavities, which have not been noticed hitherto. They are not abundant, but occur in several localities, having been found by J. P. Iddings at Forgia Vecchia, and in the obsidian stream on Volcano, and having been noted in specimens from Monte della Guardia. The crystals at Forgia Vecchia are very thin plates, the crystallographical measurements of which are given in detail by the authors. The optical properties not only agree with orthorhombic symmetry, but also with the determinations made on the fayalite from Obsidian Cliff, in the Yellowstone Park (this vol., p. 26). The chemical composition, too, is the same in both cases, namely, orthosilicate of iron. The occurrence of fayalite in the hollow spherulites and lithophysæ in the obsidian of the Lipari Islands, whilst not so abundant as in that of the Yellowstone Park, is identical. It is associated in the same manner with tridymite and alkali felspars, and its development is due to the same causes in the two regions.

B. H. B.

Two New Meteoric Irons. By F. P. VENABLE (*Amer. J. Sci.*, **40**, 161—163).—1. A mass is reported to have fallen in 1846 at Deep Springs Farm, in Rockingham Co., North Carolina. It is now in the possession of the State Museum. The weight of the mass was 11·5 kilos. It had the shape of a rhomboid, and was coated with oxidation products, giving it a dull-reddish colour. The surface is irregularly pitted. On being polished and etched, it faintly exhibited Widmanstätten figures. It belongs to the class of sweating meteorites, beads of deliquesced ferric chloride appearing on the surface. The analysis gave—

Fe.	P.	SiO_2.	Cl.	Ni.	Co.	Total.
87·01	0·04	0·53	0·39	11·69	0·79	100·45

2. A meteoric iron was found in 1889 in Henry Co., Virginia. It weighed 1·7 kilos., and the detached pieces, mainly crust, 0·22 kilo. The iron contains a considerable amount of ferric chloride, and rapidly crumbles. On polishing one of the sides, the Widmanstätten figures came out plainly, no etching being necessary. The analysis gave the following results:—

Fe.	Cl.	SiO_2.	P.	Co.	Ni.	Total.
90·54	0·35	0·04	0·13	0·94	7·70	99·70

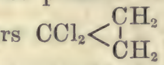
B. H. B.

Organic Chemistry.

Action of Chlorine on Trimethylene. By G. GUSTAVSON (*J. pr. Chem.* [2], **42**, 495—500).—Chlorine has hardly any action on trimethylene in the dark, but explodes with it in direct sunlight. Chlorine was passed into a globe ($7\frac{1}{4}$ litres) containing the trimethylene (7 litres) and water; the globe was kept cool, and the oil allowed to collect in a separating funnel ground into the neck. The oil consisted almost entirely of dichlorotrimethylene.

Dichlorotrimethylene, $C_3H_4Cl_2$, is a colourless liquid of peculiar odour; it boils at 75° (746 mm.), and is nearly insoluble in water. Its chemical stability is great; nitric acid decomposes it with difficulty; water at 180—190° has scarcely any action on it, and it can be distilled over sodium, which only acts on it at 160—165°, producing substances still under investigation. When dichlorotrimethylene and bromine (equal mols.) are sealed in a tube and exposed to sunlight for 4—5 summer days, or heated at 140—150° for 3—4 hours, the *dibromide*, $C_3H_4Cl_2Br_2$, is produced; it is a heavy, colourless liquid which boils almost without any decomposition at 203—207° (770 mm.).

Allylene dichloride is the only compound of the formula $C_3H_4Cl_2$ which boils at 75°; that dichlorotrimethylene is not identical with this is shown by the fact that the dibromo-compound obtained from allylene dichloride boils at 190° (Friedel and Silva; 188°, Pinner).

Of the three possible formulæ for this dichlorotrimethylene, the author favours  $CCl_2<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$; for the dibromide approximates in boiling point to α-epidichlorhydrin dibromide, $CH_2Cl{\cdot}CClBr{\cdot}CH_2Br$, and therefore, probably, has a similar structure. A. G. B.

Hexylene Dibromide obtained from Diallyl. By N. DEMYANOFF (*J. Russ. Chem. Soc.*, **22**, 117—118).—In order to prepare hexylene dibromide, well cooled diallyl (b. p. 59—60°) was saturated with hydrogen bromide, when a mixture of a solid with a liquid was obtained. After washing with water, the two compounds were separated by filtration and suction. The liquid product was a hexylene dibromide boiling at 212—220° with decomposition. The solid product, after recrystallisation from ether, was obtained in large, rhombic scales melting at 38—39°, and boiling almost without decomposition at 210°. The author considers the liquid compound to be $CH_2Br{\cdot}[CH_2]_4{\cdot}CH_2Br$, and the solid as $CHMeBr{\cdot}CH_2{\cdot}CH_2{\cdot}CHMeBr$, and that diallyl is a mixture of two (geometrical) isomerides.

B. B.

Oxidation of Potassium Cyanide with Potassium Permanganate. By J. VOLHARD (*Annalen*, **259**, 377—380).—Carbamide can be very conveniently prepared in moderately large quantities in the following manner:—A solution of potassium permanganate (63 grams) in water (1 litre) is gradually added to a solution of potassium cyanide (39 grams) and potassium hydroxide (10 grams) in water (100 c.c.), the temperature being kept below 17°; but it is unnecessary to wait until the pink colour has disappeared before continuing the addition of the permanganate. The solution is then placed in cold water for seven to eight hours until it becomes colourless, mixed with a concentrated solution of ammonium sulphate (70 grams), heated to boiling, and filtered; the precipitate is washed with boiling water, the filtrate and washings evaporated to dryness, and the carbamide extracted with 95 per cent. alcohol. The yield is 68 per cent. of the theoretical, but the product still contains a little ammonium chloride and traces of the sulphate, from which it can most easily be freed by treating its aqueous solution with a little precipitated barium carbonate, evaporating to dryness, and then extracting with absolute alcohol. F. S. K.

Combination of Mercuric Cyanide with Cadmium Salts. By R. VARET (*Compt. rend.*, **111**, 679—681).—Powdered mercuric cyanide, 25 parts, is gradually added to a boiling concentrated solution of cadmium iodide, 30 parts, and the liquid is filtered and allowed to evaporate over sulphuric acid. The compound $HgCy_2,CdCy_2,HgI_2 + 7H_2O$ separates in transparent lamellæ, which alter rapidly when exposed to air, and dissolve in water and ammonia. It becomes anhydrous at 110°, and at the same time decomposes with liberation of mercuric iodide. Dilute acids decompose it with liberation of mercuric iodide and hydrocyanic acid, while mercuric cyanide and the cadmium salt of the particular acid used remain in solution. When heated with a solution of cupric sulphate, cyanogen is evolved, and a precipitate of the composition Cu_2Cy_2,HgI_2 is formed. These facts show that all the cyanogen is not combined with the mercury, and that the salt is not simply a compound of cadmium iodide with mercuric cyanide.

Cadmium bromide (18 parts), added gradually to a boiling solution of mercuric cyanide (25 parts), yields slender needles of the compound $2HgCy_2,CdBr_2 + 4\frac{1}{2}H_2O$, which alters but little when exposed to air, dissolves in water and in ammonia, and becomes anhydrous at 100°. Dilute acids liberate hydrocyanic acid, but no mercuric bromide sublimes when the salt is gently heated; but when more strongly heated, cyanogen and mercury are evolved and some mercuric cyanide sublimes. It follows that the salt is a compound of mercuric cyanide and cadmium bromide.

If a solution containing 25 parts of mercuric cyanide and 30 parts of cadmium bromide is gently evaporated on a water-bath, the salt $HgCy_2,CdBr_2,3H_2O$ separates in small, very hard, granular crystals which alter but little when exposed to air, become anhydrous at 100°, and are less soluble in water and in ammonia than the preceding compound.

If a concentrated solution of 20 parts of cadmium chloride is added drop by drop to a saturated solution of 25 parts of mercuric cyanide, heated at 80°, and the liquid is slowly concentrated after addition of sufficient warm water to dissolve the white precipitate which forms, the compound $HgCy_2,CdCl_2 + 2H_2O$ separates in small, granular crystals. It is soluble in water and in ammonia, is decomposed by dilute acids, and becomes anhydrous at 110°. C. H. B.

Action of Alcoholic Potassium Cyanide on Halogen Derivatives of Amylene. By C. HELL and M. WILDERMANN (*Ber.*, **23**, 3210—3215).—It is well known that whereas the primary dibromides of normal olefines are readily converted into the corresponding dinitriles, the derivatives of the iso-compounds only give very small yields on treatment with alcoholic potassium cyanide. Thus isoamylene bromide forms, besides the dinitriles, large quantities of bromamylene and of humous substances. The authors find that the reaction takes place more readily if isoamylene chloride is employed in place of the bromide, and the mixture is heated in a sealed tube at 180°. The nitrile formed gave on hydrolysis a crystalline acid seemingly identical with the trimethylsuccinic acid obtained by

Schad (*Inaug. Diss.*, *Berne*, 1886), and an oily acid which could not be obtained crystalline. The yield of both these acids was better than that given by the bromide.

It was also found that addition of hydrochloric acid to the mixture of isoamylene chloride and alcoholic potassium cyanide causes a great increase in the quantity of humous substance formed, whence it would appear that the formation of the latter is due to the action of hydrochloric acid on the hydrocyanic acid; this was confirmed by adding hydrochloric acid to an alcoholic solution of potassium cyanide which had previously been boiled for some time without undergoing alteration, when, after a few minutes, a copious separation of humus took place. Hence all those substances which readily lose hydrogen chloride or bromide by the action of potassium cyanide will give large quantities of humus, owing to the action of the acid thus set free on the hydrocyanic acid, azulmic and hydrazulmic acids being formed.

When isoamylene bromide is heated with bromine, it is converted into a *tribromopentane*, the most probable formula of which is $CMe_2Br\cdot CMeBr_2$. This is readily acted on by alcoholic potassium cyanide without formation of humus or of bromamylene in any quantity. The nitrile formed is almost insoluble in water and ether, but dissolves readily in alcohol. The hydrolysis is best performed by heating it in a sealed tube at 130—150° with concentrated hydrochloric acid, and extracting the product with ether. After removing the latter by evaporation, a yellowish, syrupy acid remains which gradually deposits a small quantity of needles; these after repeated crystallisation from water, melted at 96—97°, and evolved carbonic anhydride at 130—140°; the quantity of the substance was too small, however, to allow of its being obtained in a pure condition. The syrupy acid, after purification by successive conversion into the calcium, barium, and silver salts, was obtained as a pale-yellow syrup which did not crystallise, even when kept for some time; it has the composition of a trimethylsuccinic or dimethylglutaric acid, but its exact constitution has not yet been determined. It only evolves minimal quantities of carbonic anhydride on heating, due to the presence of traces of the above crystalline acid. H. G. C.

Derivatives of Melidoacetic Acid. By R. Krüger (*J. pr. Chem.* [2], **42**, 473—494; compare this Journal, 1875, 1184).—Melidoacetic acid is best obtained as follows:—10 grams of sodium is dissolved in alcohol, the solution cooled and mixed with a solution of cyanamide (20 grams) in alcohol (40 c.c.); an equal volume of ether is then added, and the resulting precipitate is heated with a mixture of cyanamide (10 grams) dissolved in alcohol (20 c.c.) and ethyl chloracetate (30 grams) for 6 to 8 hours in a reflux apparatus. The whole is then dissolved in dilute soda, filtered, and the melidoacetic acid precipitated by acetic acid; it is purified by dissolving it in dilute hydrochloric acid and passing hydrogen chloride into the cooled solution, when its hydrochloride separates in large needles which are recrystallised and decomposed by adding ammonia to the aqueous solution. The *potassium*, *sodium*, *calcium*, and *barium* salts were obtained.

Ammelidoacetic acid, $C_3N_3(OH)_2\cdot NH\cdot CH_2\cdot COOH$, is obtained by heating melidoacetic acid with excess of barium oxide and water in a reflux apparatus until no more ammonia is evolved, and crystallising the portion which remains undissolved from hot hydrochloric acid. It crystallises in rhombic or monoclinic tables, and dissolves freely in hot water, but not in alcohol. The *copper salt*, $(C_5H_5N_4O_4)_2Cu + 6H_2O$, crystallises in dark-blue, rhombic tables; the *silver salt* is a white precipitate of uncertain composition: the *basic lead salt*, $C_5H_4N_4O_4Pb$, crystallises in transparent crystals which are insoluble in water: the *barium salt*, $C_{20}H_{34}N_{16}O_{24}Ba_3 + 8H_2O$, crystallises in long, rhombic tables, soluble in much hot water; the *strontium salt*, $C_{10}H_{10}N_8O_8Sr + 4H_2O$, forms rhombic or monoclinic tables; the *calcium salt*, which was obtained like the last two salts, namely, by adding calcium hydroxide to a solution of the acid, precipitating the excess of calcium with carbonic anhydride, filtering, and crystallising, forms crystals which are similar to the strontium salt, but have an uncertain composition; the *calcium salt*, $C_{10}H_{10}N_8O_8Ca + 4H_2O$, obtained by mixing the calculated quantities of calcium oxide and ammelidoacetic acid and crystallising, forms glistening, quadratic prisms; the *sodium*, *potassium*, and *ammonium* salts (each with 2 mols. H_2O) are of normal composition, and easily soluble in water.

Cyanuracetic acid, $C_3N_3(OH)_2\cdot O\cdot CH_2\cdot COOH$, is obtained when melidoacetic acid is heated in a sealed tube with strong hydrochloric acid at 180° for several hours until it has all dissolved; when the tube is opened the liquid froths up from the escape of gas, and after a time the new acid crystallises out, together with ammonium chloride, from which it is separated by its solubility in absolute alcohol. It crystallises (with 1 mol. H_2O) in prisms and needles, and dissolves very freely in water. There are three series of salts: the *copper salt*, $C_{10}H_8N_6O_{10}Cu + 2H_2O$; the *silver salt*, $C_5H_2N_3O_5Ag_3 + H_2O$; the *barium salt*, $C_5H_3N_3O_5Ba + 2H_2O$, and the *potassium salt*, $C_5H_4N_3O_5K + H_2O$, are here described; the *ethyl salt*, $C_5H_4N_3O_5Et$, crystallises in silky needles which melt at 208° and solidify at 195°.

Cyanuracetic acid is synthetically obtained by heating disodium cyanurate with sodium chloracetate in aqueous solution.

A. G. B.

Two New Butyl Nitrates. By G. Bertoni (*Gazzetta*, **20**, 372—376).—Of the four theoretically possible butyl nitrates, only one, the isoprimary salt, has hitherto been prepared (Wurtz, *Compt. rend.*, 1854).

The normal primary nitrate, $CH_2Pr^{\alpha}\cdot NO_3$, is prepared by adding quantities of 10 c.c. of pure normal butyl alcohol, drop by drop, to a strongly cooled mixture of 2 vols. of sulphuric acid (sp. gr. = 1·85) and 1 vol. of nitric acid (sp. gr. = 1·4), and proceeding as in the manufacture of nitroglycerol. It is a colourless liquid, with a pleasant ethereal odour and a sweet taste, which becomes pungent after a time. It boils at 136°, and its sp. gr. at 0° is 1·048. It dissolves in alcohol, ether, acetic acid, carbon bisulphide, &c., but not in water. With acids, it behaves like other ethereal nitrates. It burns with an olive-green flame, and explodes with violence when heated in a sealed tube to a higher temperature than its boiling point.

Secondary butyl nitrate, CHEtMe·NO_3, is prepared like the preceding compound, the temperature being carefully kept below 0° during the whole of the reaction. It is a colourless, mobile liquid, with a pleasant, penetrating odour, boils at 124°, and has a sp. gr. of 1·0382. It dissolves in most organic solvents, but not in water. It is more readily decomposed than its isomerides by sulphuric or hydrosulphuric acid. Its vapour explodes when superheated. S. B. A. A.

Action of Hydrogen Chloride and Bromide on Ethyl Allyl Ether. By S. N. KIJNER (*J. Russ. Chem. Soc.*, **22**, 27—32).—The author has made attempts to convert ethyl allyl ether into ethyl propyl ether by acting on it with hydrogen bromide, but the result was quite different when ethyl allyl ether, saturated with hydrogen bromide at —15°, was heated in a sealed tube at 30—40° for 10 hours; it was found to be decomposed with formation of allyl bromide and ethyl bromide, this reaction taking place to some extent even at —15°. Hydrogen chloride and allyl ethyl ether in like manner yield allyl and ethyl chlorides, but the reaction requires more time and a higher temperature. This result accords with the fact that the reaction takes place with development of heat. This is evident from the thermochemical data, and the reaction will be more energetic with the gaseous acids than with the aqueous solution, as more heat is developed by the action in the first case than in the second.

B. B.

Tetramethylene Glycol. By P. J. DEKKERS (*Rec. Trav. Chim.*, **9**, 92—102; see also Abstr., 1889, 950).—Tetramethylene glycol is the only dihydroxy-derivative of normal butane which has not been prepared up to the present time. The author endeavoured to obtain its dibenzoate by the action of sodium on chlorethyl benzoate, C_2H_4·Cl·OBz, but only obtained a mixture of sodium chloride, sodium benzoate, and ethylene benzoate. The action of sodium and silver nitrite on a solution of tetramethylenediamine sulphate or oxalate also gave negative results, although with the former salt a liquid was obtained which was possibly tetramethylene oxide.

The following method was then adopted with more satisfactory results. Tetramethylenediamine, when mixed with methyl carbonate in the cold, gradually deposits white crystals of *methyl tetramethylenediamidoformate*, $C_4H_8(NH{\cdot}COOMe)_2$, which, after recrystallisation from water, melt at 128°. When the latter is treated with five times its weight of cold absolute nitric acid, it yields *methyl tetramethylenedinitramidoformate*, $C_4H_8[N(NO_2){\cdot}COOMe]_2$, which separates from alcohol in crystals melting at 61—62°. To convert this into the nitramine, it is warmed with ammonia, the solution precipitated with acetic acid, the precipitate washed with cold water, and recrystallised from the hot liquid. The *tetramethylenedinitramine*, $C_4H_8(NH{\cdot}NO_2)_2$, thus obtained forms hard crystals melting at 163°, which are fairly soluble in hot water. When it is warmed on the water-bath with very dilute sulphuric acid, a volatile liquid distils over, and a gas is formed which is partially absorbed by hydrobromic acid with formation of tetramethylene bromide, and by bromine with formation of butine tetrabromide. The unabsorbed gas consists of nitrous oxide. When the residual liquid in the flask is distilled under reduced pressure it yields *tetramethylene glycol*, $C_4H_8(OH)_2$, as a thick, colourless liquid which boils at 203—205° under 752 mm., and at 152—153° under 120 mm. pressure, and yields succinic acid on oxidation. When shaken with benzoic chloride and soda solution, it yields the *dibenzoate*, $C_4H_8(OBz)_2$, melting at 81—82°.

As mentioned above, a volatile liquid distils over when tetramethylenenitramine is warmed with dilute sulphuric acid. This separates into two layers, the upper one consisting of a liquid boiling at 67°, and the lower of an aqueous solution of a liquid boiling at 83—88°. These have not been closely examined, but the former probably is tetramethylene oxide. H. G. C.

Starch. By K. ZULKOWSKI (*Ber.*, **23**, 3295—3297).—Starch dissolves in hot glycerol, and is converted into the soluble modification; by further heating and treatment with alcohol, erythrodextrin and achroodextrin are obtained free from sugar; from the alcoholic filtrate, two soluble carbohydrates may be separated by treatment with barium hydroxide, absolute alcohol, and anhydrous ether; the second of these remains dissolved in the ether-alcohol, and may be precipitated by means of barium hydroxide.

From the extreme difficulty experienced in removing the glycerol, the author suggests that it may take part in the reaction.

J. B. T.

α- and β-Amyrin. By A. VESTERBERG (*Ber.*, **23**, 3186—3190; see also Abstr., 1887, 733). The elemi resin employed in these researches, after trituration with alcohol, showed, under the microscope, numerous crystals of amyrin, together with a few isodiametric crystals of elemic acid. The total amount of α- and β-amyrin is 20—25 per cent., a large portion of the residue being of an alcoholic nature, as it is acted on by acetic anhydride. The empirical formula of both α- and β-amyrin was found, from analysis and determination of the hydrolysis equivalent of their acetates, to be $C_{30}H_{50}O$. The compounds are extremely similar, and form slender, elastic, silky needles which are readily soluble in benzene, ether, acetic acid, and hot alcohol, sparingly in cold alcohol and light petroleum. The ratio of their solubility in alcohol at 19—19·5° is 3 : 5·12. α-Amyrin melts at 181—181·5, and rotates the plane of polarisation to the right, $[\alpha]_D = +91·59°$, whilst β-amyrin melts at 193—194°, and rotates the plane of polarised light more strongly to the right, $[\alpha]_D = 99·81°$.

Both compounds, unlike cholesterin and lactucerol, crystallise from aqueous alcohol without water of crystallisation. They are probably secondary alcohols, as they give acetyl and benzoyl derivatives, and on oxidation yield α- and β-amyron, which are probably ketones. Phosphorus pentachloride converts them into dextrorotatory hydrocarbons, $C_{30}H_{48}$, which may be termed amyrilenes. Phosphorus pentoxide, on the other hand, yields with α-amyrin a lævorotatory amyrilene.

α- and *β-Amyrin acetates*, $C_{30}H_{49}OAc$, are formed in the separation of the amyrins (*loc. cit.*), but are only obtained pure by repeated crystallisation from light petroleum or benzene. Both are sparingly soluble in alcohol and ether, readily in light petroleum, and more easily in benzene and chloroform. The α-compound crystallises in large plates, melts at 221°, and has a sp. rot. power $[\alpha]_D = +77°$. The β-compound forms long, prismatic crystals melting at 236°, and having a sp. rot. power $[\alpha]_D = 78{\cdot}6°$. Both are oxidised by chromic acid to oxyamyrin acetates, $C_{36}H_{47}O_2Ac$.

The α- and *β-amyrin benzoates* are obtained by heating α- and β-amyrin with benzoic chloride at 130°. The α-compound is crystallised from alcoholic ether, and is sparingly soluble in alcohol, more readily in ether, and very easily in light petroleum and benzene. The β-compound, after recrystallisation from light petroleum, is almost insoluble in cold alcohol, sparingly soluble in ether and cold light petroleum, readily in the hot liquid and in benzene.

When α- and β-amyrin acetates are dissolved in chloroform or carbon bisulphide, and bromine added, either alone or diluted with acetic acid, the solutions are coloured brownish-yellow, and hydrogen bromide is evolved. The crystalline masses which remain after spontaneous evaporation are recrystallised from benzene (α) or light petroleum (β), and the finely-powdered bromacetates treated with alcoholic potash.

Brom-α-amyrin, $C_{30}H_{48}Br{\cdot}OH$, melts at 177—178°, is sparingly soluble in cold acetic acid and alcohol, readily in benzene, and almost insoluble in light petroleum; it is dextrorotatory, and has a sp. rot. power $[\alpha]_D = +72{\cdot}8°$. Its *acetate*, $C_{30}H_{48}Br{\cdot}OAc$, crystallises from benzene in six-sided plates or flat prisms, containing benzene of crystallisation, which is evolved when the crystals are allowed to remain in the air. It has not, however, been obtained quite pure, but appears to melt at about 268°; the bromine is not removed by alcoholic potash, ammonia, or aniline.

Brom-β-amyrin could not be obtained crystalline, the warm solutions in alcohol, benzene, and light petroleum solidifying to jellies. It is very soluble in hot acetic acid and benzene, less readily in alcohol and light petroleum. After drying at 98°, it melts at 182—186°. The *acetate* forms prismatic crystals, readily soluble in chloroform and benzene, sparingly in light petroleum, which, after recrystallisation from the latter, melt at 238°. As it is fairly soluble in hot light petroleum, it may be thus easily separated from the brom-α-acetate, and can, therefore, be prepared directly from the mixture of amyrins. H. G. C.

Isopropylamines. By H. MALBOT and A. MALBOT (*Compt. rend.*, **111**, 650—652).—The action of isopropyl iodide on an equivalent quantity of highly concentrated aqueous ammonia, at the ordinary temperature, is very slow, but is complete, the product consisting entirely of isopropylamine hydriodide. At 100°, the action is still slow, and requires about four days before it is complete. The chief product is isopropylamine hydriodide, but a small quantity of the diamine is also formed. Ammonium iodide is formed in quantity larger than that corresponding with the quantity of diamine, a result due to the liberation of some propylene. At 120—130°, and at

140—155°, the chief product is still the monamine, mixed with a small quantity of diamine, the proportion of the latter being practically the same in both cases. The quantity of propylene liberated is, however, considerably greater at the higher temperature. The quantity of diisopropylamine hydriodide does not exceed a certain value, because it reacts with the monamine, with elimination of propylene.

Isopropyl chloride reacts with aqueous ammonia at 140°, and the monamine is mixed with some diamine, but the change is far from complete, because the amines are present partly in the free state. In this respect isopropyl chloride differs from isopropyl iodide, and more nearly resembles orthopropyl, isobutyl, and isoamyl chlorides, which yield the free amines. There is, however, this difference, that whilst it is easy to obtain tripropyl-, triisobutyl-, and triiso-amylamines, diisopropylamine is the final term in the action of ammonia on the haloïd salts of isopropyl. C. H. B.

Propylnitramine and Isopropylnitramine and their Derivatives. By J. C. A. Simon Thomas (*Rec. Trav. Chim.*, **9**, 69—91).—Propylnitramine and isopropylnitramine are readily obtained in a similar manner to methylnitramine (Franchimont and Klobbie, Abstr., 1888, 492). The propylamine and isopropylamine required for their preparation were obtained by Hoogewerff and van Dorp's method (Abstr., 1887, 245; 1888, 1194), and converted into the corresponding amidoformates by the action of methyl chloroformate in 25 per cent. aqueous solution, extraction with ether, and fractionation. *Methyl propylamidoformate*, $NHPr^{\alpha}\cdot COOMe$, is a colourless liquid, which has a faint penetrating odour, and boils at 180° under 755 mm. pressure. Its sp. gr. is 0·992 at 15°. *Methyl isopropylamidoformate*,

$$NHPr^{\beta}\cdot COOMe,$$

is likewise a colourless liquid, having a faint penetrating odour, which boils at 165·5° under 760 mm. pressure, and has a sp. gr. of 0·981 at 15°. Both compounds are readily converted into the nitro-derivatives by gradually adding them to cooled absolute nitric acid, with continuous shaking. In the case of the isopropyl compound, cooling with ice and very gradual addition of the amidoformate, is necessary, as otherwise oxidation readily takes place. The acid solution is then, in both cases, poured on to soda crystals covered with a little water, the yellowish liquid which separates taken up with ether, the ether distilled off, and the residual liquid dried over sulphuric acid. *Methyl propylnitramidoformate*, $NO_2\cdot NPr^{\alpha}\cdot COOMe$, is thus obtained as an almost colourless liquid, which has a sweetish odour, and does not solidify at −20°. It has a sp. gr. of 1·187 at 15°, and evolves gas when heated at 139°. *Methyl isopropylnitramidoformate*, $NO_2\cdot NPr^{\beta}\cdot COOMe$, has a sp. gr. of 1·1585 at 15°, and commences to decompose at 120°.

To convert these compounds into the nitramines, dry ammonia gas is passed into their ethereal solutions. The ammonium salt of propylnitramine is precipitated as a crystalline mass, which is collected, washed with ether, decomposed by sulphuric acid, and the propylnitramine extracted with ether. After evaporating off the ether and drying the residue over sulphuric acid, *propylnitramine*, $NHPr^{\alpha}\cdot NO_2$, is obtained as a colourless, inodorous liquid, which cannot be distilled without decomposition at the ordinary pressure, but boils at 128—129° under 40 mm. pressure. It has a sp. gr. of 1·102 at 15°, decomposes at 142°, and solidifies between −21° and −23°, and is not coloured on exposure to light. Its aqueous solution has an alkaline reaction, and gives a precipitate with many salts of the heavy metals. The *potassium* salt, $NPr^{\alpha}K\cdot NO_2$, obtained by acting on the nitramine with the theoretical quantity of alcoholic potash, forms small, nacreous, hygroscopic plates, and the *silver* salt, $NPr^{\alpha}Ag\cdot NO_2$, crystallises in small, slender needles, which blacken in the light.

Isopropylnitramine, $NHPr^{\beta}\cdot NO_2$, is obtained in the same manner as the normal compound, but must be further purified by dissolving it in potassium carbonate solution, extracting the latter with ether, and acidifying the residual solution with sulphuric acid. It is a colourless compound which melts at −4°, distils at 90—91° under 10 mm. pressure, commences to decompose at 150°, and has a sp. gr. of 1·098 at 15°. It is scarcely soluble in water, but mixes with alcohol and ether in every proportion. The *potassium* salt, $NPr^{\beta}K\cdot NO_2$, forms long, slender, very hygroscopic needles, and the *silver* salt, $NPr^{\beta}Ag\cdot NO_2$, crystallises in thin plates.

When the potassium salts of these nitramines are treated with an alkyl bromide, or the silver salts with an alkyl iodide in alcoholic solution, dialkylnitramines are obtained. The following have been prepared in this manner :—*Dipropylnitramine*, $NPr^{\alpha}{}_2\cdot NO_2$, a colourless liquid boiling at 76—79° under 10 mm. pressure; *di-isopropylnitramine*, $NPr^{\beta}{}_2\cdot NO_2$, boiling at 55—57° under 10 mm. pressure; *propylisopropylnitramine*, $NPr^{\alpha}Pr^{\beta}\cdot NO_2$, boiling at 65—68° under the same pressure; and *benzylpropylnitramine*, $NO_2\cdot NPr^{\alpha}\cdot CH_2Ph$, melting at 8—10°, and boiling at 200—205° under 40 mm. pressure. The first three compounds do not solidify in a mixture of solid carbonic anhydride and ether. The silver and potassium salts of propylnitramine, unlike the corresponding methyl derivatives, do not yield a picryl compound on treatment with picric chloride, the latter being simply converted into silver or potassium picrate. Ethyl and isopropylnitramine behave in a similar manner.

When the silver salts of the nitramines are warmed with acetic or benzoic chloride, a simple reaction does not take place. Some silver chloride is precipitated, and nitrous oxide is evolved. It appears probable that the acetyl or benzoyl compound is first formed, and then splits up into propyl acetate or benzoate and nitrous oxide :—

$$CH_3\cdot CO\cdot NPr^{\alpha}\cdot NO_2 = CH_3\cdot COOPr^{\alpha} + N_2O.$$

The author has succeeded in isolating propyl benzoate from the product of the reaction with benzoic chloride.

The molecular weights of picrylmethylnitramine (Abstr., 1886, 455) and of isopropylnitramine have been determined by Raoult's method, the results agreeing with the formulæ above ascribed to them.

H. G. C.

Amylamines. By A. Berg (*Compt. rend.*, **111**, 606—608).—Amyl chloride and saturated aqueous ammonia are mixed in equivalent proportions, and sufficient alcohol of 92° is added to completely dissolve the mixture. The liquid is heated at 110—120° for eight or nine hours, poured off from the crystals of ammonium chloride (mixed with a small quantity of diamylamine hydrochloride), acidified with hydrochloric acid, and distilled, to remove alcohol and unaltered amyl chloride. The residual liquid, when allowed to cool, deposits nacreous plates of diamylamine hydrochloride, which can be almost completely separated by successive concentrations. If recrystallised from boiling water after treatment with animal charcoal, it is obtained in perfectly pure, large plates, with a micaceous lustre.

The mother liquor from the diamylamine hydrochloride is evaporated to dryness and made alkaline with potash or soda; the liberated base consists of almost pure amylamine mixed with a very small quantity of the di- and tri-amine, the proportions in which the three bases are obtained from the original product being monamine 6 parts, diamine 9 parts, triamine ½ to 1 part. The same result is obtained with only half the quantity of alcohol. Alcoholic ammonia yields similar results, but the diamine is formed in still larger proportions.

Pure amylamine is obtained by the method of Duvillier and Buisine. A dilute aqueous solution is mixed with a suitable quantity of ethyl oxalate, a rise of temperature being avoided; diamyloxamide is precipitated, and is almost completely insoluble in water. The mother liquor, when concentrated, yields amylamine amyloxamate, $C_5H_{11}\cdot NH\cdot CO\cdot COOH,NH_2\cdot C_5H_{11}$, very soluble in hot water, but much less soluble in cold water, and easily decomposed by aqueous potash, which has very little action on diamyloxamide. With calcium chloride, amylamine amyloxamate yields a precipitate of calcium amyloxamate, which crystallises readily from hot water in small, brilliant, hydrated lamellæ. C. H. B.

Diethylenediamine. By A. W. v. Hofmann (*Ber.*, **23**, 3297—3303).—Diethylenediamine purified by treatment with sodium melts at 104°, boils at 145—146°, and solidifies on cooling, forming a hard, white, crystalline mass, which is extremely soluble in water, and is deposited from absolute alcohol in large, transparent crystals. The *benzoyl* derivative is deposited from alcohol in rhombic crystals which melt at 191°. A technical product termed "spermin," "piperazidin," or "piperazin" is found to be identical with diethylenediamine (compare Sieber, Abstr., 1890, 476). J. B. T.

Action of Zinc and Ethyl Chloracetate on Ketones and Aldehydes. By S. Reformatsky (*J. Russ. Chem. Soc.*, **22**, 44—64).—Acetone, when treated with ethyl chloracetate and zinc, gives a product which, on decomposition with water yields the β-dimethylethylenelactic acid (hydroxyvaleric acid), $OH\cdot CMe_2\cdot CH_2\cdot COOH$, of M. and A. Saytzeff. Methyl propyl ketone, under similar conditions, yields *β-methylpropylethylenelactic acid*, $OH\cdot CMePr\cdot CH_2\cdot COOH$. This, on distillation with dilute sulphuric acid, yields *methylpropylacrylic acid*, $CMePr\colon CH\cdot COOH$. Diethyl ketone, when similarly treated, yields

Shinokoff's β-diethylethylenelactic acid, $OH{\cdot}CEt_2{\cdot}CH_2{\cdot}COOH$. By distillation with dilute sulphuric acid, this acid loses the elements of water, and *β-diethylacrylic acid*, $CEt_2{:}CH{\cdot}COOH$, is obtained. The above reaction when applied to butyrone gives rise to Shinokoff's β-dipropylethylenelactic acid, $OH{\cdot}CPr_2{\cdot}CH_2{\cdot}COOH$, which, on losing the elements of water, is converted into Albitzky's dipropylacrylic acid. This acid yields a dibromide melting at 102—104°, whereas the dibromide prepared by the author from Albitzky's original acid melts at 80—82°. This difference is probably due to geometrical isomerism, as the compounds contain an asymmetrical carbon atom. The above reaction may be represented by the general scheme, $RR_1CO + CH_2Cl{\cdot}COOEt + Zn = CRR_1(OZnCl){\cdot}CH_2{\cdot}COOEt$, and this with $3H_2O$ gives $RR_1{:}C(OH){\cdot}CH_2{\cdot}COOH$. Analogous results obtained with aldehydes will be communicated in a future paper. B. B.

Action of Phosphorus Trichloride on Organic Acids and Water. By C. H. Bothamley and G. R. Thompson (*Chem. News*, **62**, 191).—Thorpe showed (Trans., 1880, 186) that the equation $3CH_3{\cdot}COOH + 2PCl_3 = 3CH_3{\cdot}COCl + P_2O_3 + 3HCl$ represented the action of phosphorus trichloride on acetic acid. The authors agree that this does represent the fundamental change (which is similar for other monobasic organic acids), and therefore true within certain narrow limits, but with excess of either reagent various secondary reactions take place, which increase with other acids of the series, as the molecular weights become greater and the volatility of the products less. With benzoic acid and phosphorus trichloride, secondary changes take place to a very considerable extent. In fact, this reaction cannot be regarded, as it hitherto has been, as a good method for preparing acid chlorides. Even the action of phosphorus as trichloride on water, which is as follows, $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$, as long as the water is in considerable excess, is disturbed by various secondary reactions as soon as the phosphorus chloride is in excess, giving rise to the formation of yellow phosphorus oxide and other oxides, including the soluble form of the oxide P_4O, which becomes insoluble at 70°; the yellow oxide was also produced in the other cases given above. Various conditions affect these changes, especially temperature. D. A. L.

Paracrylic and Hydracrylic Acids. By E. Klimenko (*J. Russ. Chem. Soc.*, **22**, 100—102).—The author's method of preparing paracrylic acid by the action of silver oxide on β-iodopropionic acid yields larger quantities of the pure acid with difficulty only. The author's improved method consists in evaporating hydracrylic acid with hydrochloric acid on the water-bath. On treating paracrylic acid with an excess of bromine, it yields bromopropionic acid. When paracrylic acid is heated with water at 100° for six hours, it is converted into an acid $C_3H_6O_3$, having the composition of hydracrylic acid. By the action of phosphorus pentachloride on hydracrylic acid, a chloride is produced, which with alcohol yields ethyl β-chloropropionate. B. B.

β-Chlorocrotonic Acids. By W. Autenrieth (*Annalen*, **259**, 358—362).—The sodium salt of β-chlorocrotonic acid, unlike the free acid, does not undergo intramolecular change when it is heated at 170—180° for 12 hours, but is almost completely decomposed into allylene, sodium chloride, and carbonic anhydride; the sodium salt of β-chlorisocrotonic acid is completely decomposed under the same conditions yielding the same products as the isomeride. F. S. K.

Preparation and Properties of Ethyl Sodacetoacetate and Ethyl Sodethylacetoacetate. By H. ELION (*Ber.*, **23**, 3123—3124).—It has been previously shown (*Rec. Trav. Chim.*, **3**, 231) that anhydrous ethyl sodacetoacetate and anhydrous ethyl sodethylacetoacetate are readily soluble in ether, but that both compounds form a hydrate which is insoluble in ether. In preparing the anhydrous compounds by the author's method (*loc. cit.*), they are obtained in ethereal solution; this solution can be most suitably employed for carrying out reactions in which the presence of water or alcohol is to be avoided, and the anhydrous compounds can be readily obtained in a solid state by evaporating the ether at a low temperature. Otto and Rössing's statement (Abstr., 1890, 1137) that anhydrous ethyl sodacetoacetate can be obtained by keeping the hydrate over sulphuric acid is contrary to the author's experience, and Michael's assumption (Abstr., 1888, 1054) that pure anhydrous ethyl sodacetoacetate exists in two forms, one of which is soluble, the other insoluble in ether, is quite unwarranted. F. S. K.

γ-Cyanacetoacetates and their Chlorimido-derivatives. By A. HALLER and A. HELD (*Compt. rend.*, **111**, 647—650).—Ethyl γ-cyanacetoacetate, boiling at 135—138° under a pressure of 40—45 mm., is mixed with its own volume of absolute alcohol, and the mixture is added to about double the quantity of absolute alcohol saturated with hydrogen chloride and cooled to 0°. Heat is developed, ammonium chloride separates, and the liquid contains a chlorine derivative and ethyl acetodicarboxylate. If ammonium chloride does not separate, the liquid is evaporated in a vacuum, mixed with fine sand, and extracted with ether. The ethereal solution yields slender, white needles of the hydrochloride of the imido-ether of ethyl acetodicarboxylate $COOEt\cdot CH_2\cdot CO\cdot CH_2\cdot C(OEt)\dot{:}NH,HCl$, which is decomposed by water with formation of ethyl acetodicarboxylate, $CO\cdot(CH_2\cdot COOEt)_2$.

If ethyl γ-cyanacetoacetate is dissolved in two or three times its weight of methyl alcohol, and hydrogen chloride is passed into the cooled liquid, crystals are obtained which melt with decomposition at 122°, and consist of the methyl-imido-ether of ethyl acetodicarboxylate plus one molecule of hydrogen chloride. When treated with silver nitrate, half the chlorine is precipitated, but the remainder can only be removed by boiling with potash. When boiled with dilute and slightly acidified alcohol, the compound yields ammonium chloride and an oily chlorinated product.

Methyl γ-cyanacetoacetate, obtained in the same way as the ethyl compound, is a somewhat thick, colourless liquid, which rapidly becomes yellow. It boils at 217—218° under normal pressure, and at 127—128° under a pressure of 20—30 mm.; it does not solidify even at a very low temperature. When treated with hydrogen chloride in presence of methyl alcohol, it yields confused white prisms which melt with decomposition at 144°, and consist of the hydrochloride of the imido-ether of methyl acetodicarboxylate plus one molecule of hydrogen chloride. It dissolves in water and in alcohol, and with potash, acidified alcohol, and silver nitrate it behaves like the corresponding ethyl compound.

It is necessary to assume that under the conditions of experiment the alkyl cyanacetoacetate undergoes molecular change, and behaves as an unsaturated compound, the chloro-derivatives having the constitution $COOMe\cdot CH_2\cdot CH(OH)\cdot CHCl\cdot C(OMe)\colon NH,HCl$ or

$$COOMe\cdot CHCl\cdot CH(OH)\cdot CH_2\cdot C(OMe)\colon NH,HCl.$$

C. H. B.

Mesitene Lactone and Isodehydracetic Acid. By R. Anschütz, P. Bendix, and W. Kerp (*Annalen*, **259**, 148—186).—The authors have repeated a number of experiments made by Hantzsch (*Annalen*, **222**, 1) in his investigation of the condensation products of ethyl acetoacetate; they have proved that the formulæ assigned by Hantzsch to mesitene lactone and isodehydracetic acid are correct, and that the original condensation product (m. p. 61—62°) is a mixture of two substances and not a compound of the composition $C_{18}H_{22}O_9$, as was supposed by Hantzsch; they also obtained results at variance with those of Hantzsch in studying the action of ammonia and alkalis on ethyl isodehydracetate, as will be described below.

When the crude condensation product of ethyl acetoacetate is repeatedly extracted with cold chloroform or benzene and the extract mixed with light petroleum, isodehydracetic acid (m. p. 155°) is precipitated in a pure condition, and its ethyl salt and mesitene lactone remain in solution. The acid can be more easily isolated by dissolving the condensation product in a mixture of ether and chloroform and shaking the solution, with concentrated potassium carbonate; on acidifying the alkaline solution, the acid is precipitated in a pure condition, and the ethereal chloroform solution, on evaporation, yields the ethyl salt and mesitene lactone, the last-named compound being invariably produced when ethyl acetoacetate is treated with concentrated sulphuric acid.

Ethyl isodehydracetate and mesitene lactone can be separated from one another by fractional distillation under a pressure of about 12 to 14 mm.; the mesitene lactone passes over at 128—130°, the ethyl salt at 166°.

Methyl isodehydracetate, $C_9H_{10}O_4$, prepared by treating the potassium salt with methyl iodide, crystallises from ether in long, colourless needles, melts at 67—67·5°, and boils at 167° under a pressure of 14 mm.; it can also be obtained, together with isodehydracetic acid and small quantities of mesitene lactone, by treating methyl acetoacetate with concentrated sulphuric acid.

When a mixture of pure ethyl isodehydracetate and the free acid is crystallised from dilute alcohol, a substance is obtained which is identical in appearance with, and has the same melting point (59—60°) as, the original condensation product.

Attempts to prepare the homomesaconic acid described by Hantzsch were unsuccessful; when ethyl isodehydracetate is hydrolysed with potash, it gives varying quantities of two new acids, melting at 221° and 149° respectively, together with oily by-products. These two acids were prepared by warming the pure ethyl salt (5 grams) on the water-bath, quickly adding a solution of potash (13 grams) in boiling water (4·5 grams), and then warming the mixture for 10 minutes; 50 grams of the ethyl salt yield 13 grams of the higher melting and 2·5 grams of the lower melting compound.

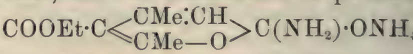
The acid melting at 221° has the composition $C_5H_6O_2$, but its molecular formula is probably $C_{10}H_{12}O_4$; it is almost insoluble in ether, benzene, chloroform, and cold water, and only moderately easily soluble in boiling water, from which it crystallises in transparent, prismatic needles melting at 221° with decomposition. The *potassium* salt, $C_{10}H_{10}O_4K_2$, is a vitreous, very hygroscopic compound. The *barium* salt, $C_{10}H_{10}O_4Ba + 4H_2O$, crystallises from cold water in spherical aggregates and is moderately easily soluble (19·1 parts of anhydrous salt in 100 parts at 20°) in water. The *copper* salt, $C_{10}H_{10}O_4Cu + 3\frac{1}{2}H_2O$, is apple-green and almost insoluble in water. The silver salt was not obtained in a pure condition. The *methyl* salt, $C_{10}H_{10}O_4Me_2$, prepared by treating the silver salt with methyl iodide, crystallises from ether in colourless, transparent prisms, melts at 71°, and is readily soluble in ether, alcohol, benzene, and chloroform, but is precipitated from the solutions on the addition of light petroleum.

The acid melting at 149° has the composition $C_8H_{10}O_3$; it crystallises from boiling water, in which it is more sparingly soluble than the acid melting at 221°, in colourless needles, and is readily soluble in alcohol, ether, and chloroform; it decomposes about 160°. The *barium* salt, $(C_8H_9O_3)_2Ba + 2H_2O$, crystallises in microscopic needles, and is very sparingly soluble in water. The *silver* salt, $C_8H_9O_3Ag$, is moderately stable in the light.

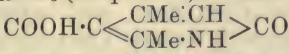
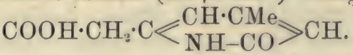
Mesitene lactam (pseudolutidostyril,) is formed in small quantities when mesitene lactone is treated with aqueous or anhydrous ammonia under various conditions. It is best prepared by passing anhydrous ammonia for 14 or 15 hours into mesitene lactone (15 grams) heated at 150 to 160°; the lactam (8·5 grams) thus produced is separated from the unchanged lactone (4·5 grams) by fractional distillation. The compound obtained in this way is identical with Hantzsch's pseudolutidostyril (Abstr., 1884, 1045, and 1885, 397). The *platinochloride*, $C_{14}H_{18}N_2O_2,H_2PtCl_6$, separates from alcohol in dark-orange, transparent crystals.

When mesitene lactone is treated with alcoholic ammonia, a small quantity of the lactam is obtained, together with ammonium carbamate and a liquid, unstable compound, the nature of which was not determined.

Anhydrous ammonia converts ethyl isodehydracetate into the corresponding lactam, which is identical with the substance (m. p. 137°) obtained by Collie (Abstr., 1887, 501) by the condensation of ethyl β-amidocrotonate.

A compound of the composition $C_{10}H_{18}O_4N_2$ is precipitated as a colourless powder when anhydrous ammonia is passed into an alcoholic ethereal solution of ethyl isodehydracetate, moisture being carefully excluded. It melts at 104° with evolution of ammonia, being reconverted into ethyl isodehydracetate, and its constitution is probably represented by the formula  $COOEt\cdot C\left<\begin{matrix}CMe{:}CH\\CMe{-}O\end{matrix}\right>C(NH_2)\cdot ONH_4$; when its concentrated aqueous solution is treated with copper chloride, a dark-green, crystalline, copper compound of the composition $(C_{10}H_{14}O_4N)_2Cu + H_2O$ is precipitated.

Ethyl isodehydracetate can be prepared by boiling ethyl sodacetoacetate with a benzene solution of ethyl chlorisocrotonate; methyl isodehydracetate can be obtained in like manner.

The synthesis of ethyl isodehydracetate in this way shows that the acid has the constitution assigned to it by Hantzsch; it is probable, therefore, that the acid obtained by Collie (*loc. cit.*) from the lactam, $C_{10}H_{13}NO_3$ (m. p. 137°), referred to above, has an analogous constitution,  $COOH\cdot C\left<\begin{matrix}CMe{:}CH\\CMe\cdot NH\end{matrix}\right>CO$, that of the acid obtained by Collie from the isomeric lactam (m. p. 165°) being probably represented by the formula  $COOH\cdot CH_2\cdot C\left<\begin{matrix}CH\cdot CMe\\NH{-}CO\end{matrix}\right>CH$. F. S. K.

Action of Methylene Iodide and Chloride on Ethyl Malonate in the Presence of Sodium Ethoxide. By S. TANATAR (*J. Russ. Chem. Soc.*, **22**, 32—39).—The experiments were undertaken with the view of obtaining an acid, $C_4H_4O_4$, isomeric or identical with fumaric or maleïc acid. The proportion of the substances taken was calculated from the equation $C_3H_2Et_2O_4 + 2Na + CH_2I_2 + 15C_2H_6O$. Sodium was dissolved in absolute alcohol and ethyl malonate was added to the solution. As on the addition of methylene diiodide, so much heat is developed that the solution will boil if care be not taken, it is advisable, to add the iodide in small portions at a time; to complete the reaction, the mixture was heated for 12 hours in a reflux apparatus. The alcohol was then removed by distillation, water added, and the oily product, which is partly soluble in water, extracted with ether. After distilling off the ether, the residue, containing some unchanged ethyl malonate and methylene iodide, was saponified with a 15 per cent. solution of potash, but part of it remained unchanged. From a solution of the potassium salt thus obtained, the acid was liberated by acidifying with hydrochloric acid and extracting with ether; the iodine was then removed from it by treatment with molecular silver. The free acid forms a honey-like syrup, which does not crystallise, but, on being kept in a desiccator for several months, becomes converted into a hard, gum-like substance. It can be further purified by converting it into the lead or silver salt and decomposing the latter with hydrogen sulphide. The calcium salt, $C_6H_8CaO_5$, is less soluble in hot than in cold water. The free acid, $C_6H_{10}O_5$, is called, by the author, *adipomalic acid*. The silver salt is $C_6H_8Ag_2O_5$; the barium salt, $C_6H_8BaO_5 + 2H_2O$.

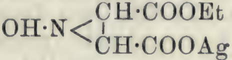
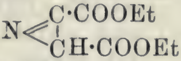
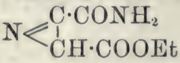
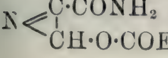
That portion of the original product of the reaction which remained unchanged on boiling with 15 per cent. potash was saponified by boiling with strong potash, the potassium salt converted into the lead salt, and this, on decomposition and saturation with lime, into a salt $C_8H_6Ca_2O_9$. From the filtrate, alcohol precipitates a calcium salt containing a little less calcium than the salt $C_6H_8Ca_2O_9$, which shows that a mixture of acids was obtained. From a second portion, iodine was removed with silver nitrate, and the silver salt, $C_8H_8Ag_4O_{10}$, was obtained, so that probably the original acids were $C_8H_{10}O_9$ and $C_8H_{12}O_{10}$. Methylene dichloride and ethyl sodiomalonate, in like manner, yielded the compound $C_4H_2Et_2O_4$, which, on hydrolysis and conversion of the potassium salt, gave the silver salt $C_8H_6Ag_4O_9$. The free acid $C_8H_{10}O_9$ crystallises in prisms which melt at 108—109°.

B. B.

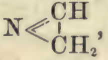
Reaction between Methylene Iodide and Ethyl Malonate. By S. TANATAR (*J. Russ. Chem. Soc.*, **22**, 39—44).—The acid $C_6H_{10}O_5$ (see preceding paper), when heated with water at 150°, undergoes no change, but if heated with hydriodic acid at 150° it yields ethyl iodide and an acid, $C_4H_6O_5$, thus:—$C_6H_{10}O_5 + HI = C_2H_5I + C_4H_6O_5$. This acid, $OH{\cdot}CH_2{\cdot}CH(COOH)_2$, the author calls (?) "*hydroxymethylmalonic acid*," whereas the original adipomalic acid, $C_6H_{10}O_5$, is regarded as *ethoxyisosuccinic acid*, $EtO{\cdot}CH_2{\cdot}CH(COOH)_2$. On heating the acid at 250°, decomposition takes place, carbonic anhydride being liberated, and a yellow oil distilling over. This is a neutral ethereal salt, which on hydrolysis yields a potassium salt, which is converted into the lead salt, $C_6H_8PbO_5$. The free acid is a thick syrup: the calcium salt is not thrown down on boiling its aqueous solution, so that the acid $C_6H_{10}O_5$ is not identical but isomeric with ethoxyisosuccinic acid, being probably dilactylic acid, as shown by the properties of the calcium and lead salts. B. B.

Succinamic Acid. By R. SERDA and J. WIEDEMANN (*Ber.*, **23**, 3284—3287).—Succinamic acid, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, prepared by treating succinimide with barium hydroxide, as described by Teuchert (*Annalen*, **134**, 139), is identical with the acid prepared by heating nitrosoglutaric acid (Wolff, *Annalen*, **260**, 114). It crystallises from hot acetone in long needles, melts at 156—157°, and is moderately easily soluble in water, but very sparingly soluble or insoluble in alcohol, benzene, and light petroleum; it is converted into ammonium succinate on prolonged boiling with water, and when heated alone at 200°, it is transformed into succinimide.

F. S. K.

Synthesis of Asparagine. By A. PIUTTI (*Gazetta*, **20**, 402—406).—When silver γ-oximidosuccinate,  $OH{\cdot}N{<}\begin{matrix}CH{\cdot}COOEt\\|\\CH{\cdot}COOAg\end{matrix}$ (Abstr., 1889, 381), is heated on the water-bath with an excess of an ethereal solution of ethyl iodide, the silver iodide removed, and the solution evaporated at 60—70°, *diethyl nitrilosuccinate*,  $N{<}\begin{matrix}C{\cdot}COOEt\\|\\CH{\cdot}COOEt\end{matrix}$ remains as a neutral, yellowish oil, which may be distilled in a vacuum with partial decomposition. When this substance is shaken with strong aqueous ammonia, *ethyl nitrilosuccinamate*,  $N{<}\begin{matrix}C{\cdot}CONH_2\\|\\CH{\cdot}COOEt\end{matrix}$ or  $N{<}\begin{matrix}C{\cdot}CONH_2\\|\\CH{\cdot}O{\cdot}COEt\end{matrix}$, is formed; this compound crystallises from alcohol or acetic acid in brilliant, rhombic plates, melts at 166—167°, and yields a bromide, $C_6H_7N_2O_3Br$, which melts with decomposition at about 140°.

On reducing an acetic acid solution of this amide with sodium amalgam (5 per cent. Na), care being taken to maintain the liquid acid, separating the bulk of the sodium acetate by crystallisation, and allowing the mother liquor to remain in prolonged contact with copper acetate, a crystalline deposit of insoluble copper salts is formed, which, on decomposition with hydrogen sulphide, yields a solution containing three asparagines. These may be obtained perfectly pure by precipitating their concentrated solution with alcohol and recrystallising from water. On leaving the mixture in a vacuum, the inactive α-compound loses its water of crystallisation and falls to powder; the β-asparagines may then be separated by their microscopic characters.

The author regards ethyl nitrilosuccinamate as a derivative of the nucleus  $N \lessdot \begin{matrix} CH \\ | \\ CH_2 \end{matrix}$, which he terms "etazole," and has prepared a long series of derivatives of nitrilosuccinamic acid in support of this view.

S. B. A. A.

Amic and Anilic Acids of Fumaric Acid and Maleïc Acid.

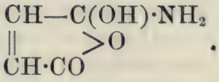
By R. Anschütz (*Annalen*, **259**, 137—148.—*Maleïnamic acid*, $C_4H_5NO_3$, is obtained when anhydrous ammonia is passed into a chloroform or benzene solution of maleïc anhydride, and the gum-like ammonium salt which is gradually precipitated warmed with water until the evolution of ammonia is at an end; on acidifying with hydrochloric acid, the maleïnamic acid is precipitated in crystals, the yield being about 70 per cent. of the theoretical. It crystallises from water in large, transparent, anhydrous plates, melts at 152—153°, and is readily soluble in hot alcohol and water, but only sparingly in hydrochloric acid, and almost insoluble in benzene, ether, and chloroform; when treated with alcoholic potash, it is converted into fumaric acid, but with aqueous alkalis and barium hydroxide in the cold, it yields salts of maleïc acid.

Fumaranilic chloride, $C_{10}H_8ClNO_2$, is obtained when fumaric chloride is treated with aniline in ethereal solution, the quantity of base employed being less than is theoretically necessary to convert the chloride into fumaric acid dianilide; the dianilide and aniline hydrochloride produced are separated by filtration, the ethereal filtrate evaporated, and the residue recrystallised from ether. Fumaranilic chloride forms transparent, yellow, prismatic needles, and melts at 119—120°; with alcohols, it yields crystalline ethereal salts, and with amines, it gives amides. When treated with cold water or dilute alkalis, it is converted into an acid of the composition $C_{10}H_9NO_3$, which melts at 230—231°, and is quite different from the fumaranilic acid (m. p. 187—187·5°) previously obtained by the author and Wirtz (Abstr., 1887, 934) from maleïnanil in like manner; the acid melting at 187—187·5° is, therefore, in future to be termed *maleïnanilic acid*, to distinguish it from the acid melting at 230—231°, which is named fumaranilic acid.

Fumaranilic acid is only sparingly soluble in boiling water, but more readily than maleïnanilic acid, and when warmed with alcoholic or aqueous potash, it is, like the latter, converted into fumaric acid.

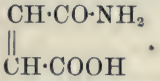
Judging from their behaviour, the amido- and anilido-derivatives of maleïc and fumaric acids have the constitution expressed by the following formulæ:—

Maleïnamic acid (m. p. 152—153°)



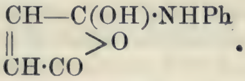
$$\begin{array}{l} CH—C(OH)\cdot NH_2 \\ \| \qquad\quad >O \\ CH\cdot CO \end{array}.$$

Fumaramic acid (m. p. 217°)



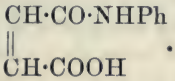
$$\begin{array}{l} CH\cdot CO\cdot NH_2 \\ \| \\ CH\cdot COOH \end{array}.$$

Maleïnanilic acid (m. p. 187—187·5)°



$$\begin{array}{l} CH—C(OH)\cdot NHPh \\ \| \qquad\quad >O \\ CH\cdot CO \end{array}.$$

Fumaranilic acid (m. p. 230—231°)



$$\begin{array}{l} CH\cdot CO\cdot NHPh \\ \| \\ CH\cdot COOH \end{array}.$$

The article concludes with a short criticism of Bischoff's paper on dynamical isomerism (compare Abstr., 1890, 723). F. S. K.

Diglycollic Anhydride. By R. ANSCHÜTZ (*Annalen*, **259**, 187—193).—*Diglycollic anhydride*, $O<\begin{smallmatrix}CH_2\cdot CO\\CH_2\cdot CO\end{smallmatrix}>O$, is obtained when finely divided diglycollic acid is boiled with acetic chloride, or when the acid is distilled under a pressure of 11 to 12 mm. It separates from warm chloroform in long, spear-shaped crystals, melts at 97°, and boils at 120° (12 mm.); it is only sparingly soluble in ether, and is readily reconverted into the acid by cold water.

Diglycollanilic acid, $C_{10}H_{11}O_4N$, is gradually deposited in crystals when an ethereal solution of the anhydride is treated with aniline; it melts at 118°. F. S. K.

Dilactylic Acid. By S. TANATAR and CH. TCHELEVIEFF (*J. Russ. Chem. Soc.*, **22**, 107—110).—It was shown by Friedel and Wurtz that calcium lactate, when heated at 270—280°, loses 1 mol. H_2O, and becomes calcium dilactate, but neither the salt nor the acid was investigated by them. The experiment was repeated by the authors, and from the calcium dilactate obtained, the free acid, $C_6H_{10}O_5$, was separated by decomposing it with oxalic acid. The syrupy liquid obtained was purified by distillation at 170°, under a pressure of 80—90 mm. The distillate, after remaining for some time in the desiccator, was converted into monoclinic, prismatic crystals melting at 105—107°, easily soluble in water, ether, chloroform, and acetic acid, but only slightly in benzene. It gives an acid potassium salt, $C_6H_9O_5K$, and a silver salt, $C_6H_8O_5Ag_2$, which, on treatment with methyl iodide, gave the methyl salt, $C_6H_8O_5Me_2$, boiling at 260°. The zinc salt, $C_6N_8O_5Zn + 3H_2O$, is amorphous. Hydriodic acid at 150° is without action on dilactylic acid. B. B.

Synthesis of Citric Acid. By A. HALLER and A. HELD (*Compt. rend.*, **111**, 682—685).—Ethyl acetodicarboxylate is prepared from ethyl γ-cyanacetoacetate in the manner previously described (this vol., p. 171), and the ethereal solution of the crude product from 10 grams of the cyanacetoacetate is converted into a cyanhydrin by cooling it in a mixture of ice and salt, adding 5 to 6 grams of finely-powdered potassium cyanide, and then, drop by drop, concentrated hydrochloric acid in quantity exactly equivalent to the cyanide. The mixture is allowed to remain in a closed vessel in a cool place for 24 hours, and is then filtered, and the ether distilled off. The cyanhydrin is boiled for two or three hours with concentrated hydrochloric acid in an apparatus with a reflux condenser, the ammonium chloride is removed and the liquid, after being concentrated to expel excess of acid, is boiled with excess of potash. The liquid now contains potassium citrate and chloride with other products formed in the course of the reactions. The citric acid is best separated by means of lead acetate, the precipitate being decomposed by hydrogen sulphide, and the citric acid extracted by means of ether.

50 grams of ethyl γ-cyanacetoacetate yield about 6·2 grams of pure citric acid, and a further quantity of about 4 to 5 grams remains in the syrupy mother liquor. C. H. B.

Action of Phosphorus Pentachloride on Citric and Aconitic Acids. By E. KLIMENKO and BUCHSTAB (*J. Russ. Chem. Soc.*, **22**, 96—99).—Pebal, by acting with phosphorus pentachloride on citric acid, obtained the solid hydroxychlorocitric acid and two liquid chloranhydrides. The authors have treated citric acid (1 part) with phosphorus pentachloride (3 parts) without heating; after some time, the solid contents of the vessel became converted into a liquid, which after the addition of some more citric acid became partly solid. It was then extracted with dry carbon bisulphide and Pebal's hydroxychlorocitric was left together with some citric acid; this when treated with alcohol, yielded a liquid boiling between 283° and 285°, identical with Malagutti's triethyl citrate, so that the solid chloride obtained at the beginning of the reaction is $C_6H_5Cl_3O_4$. The same chloride is contained in the liquid product of the reaction. On heating citric acid with phosphorus pentachloride, the liquid product is found to prevail, and this contains some aconitic chloride. Aconitic acid with phosphorus pentachloride gives the chloride $C_6H_3O_3Cl_3$ identical with the above bye-product, and this, on being treated with ethyl alcohol, yields Mercadante's triethyl aconitate. The formula $C_6H_6O_5Cl_2$ given to the solid chloride by Skinner and Ruhemann (Trans., 1889, 235) is contradicted by the authors, who find that the solid product is not homogeneous, but always contains citric acid and probably some aconitic acid. B. B.

Alkyl Substitution Products of Ethyl Dicarboxyglutaconate, and a New Synthesis of αα-Dialkylglutaric Acids. By M.

GUTHZEIT and O. DRESSEL (*Ber.*, **23**, 3179—3186).—The authors have already described a method by which dialkylglutaric acids containing two similar alkyl groups may be prepared (Abstr., 1889, 860). To prepare disubstituted glutaric acids containing two different alkyl groups, it is necessary to start with ethyl dicarboxyglutaconate, $CH(COOEt)_2 \cdot CH\vdots C(COOEt)_2$. When the sodium compound of this ethereal salt is heated with an excess of ethyl iodide in a sealed tube at 170—180°, it yields the *ethyl* derivative, $CEt(COOEt) \cdot CH\vdots C(COOEt)_2$, as a colourless oil boiling without decomposition at 195—202° under 11 mm. pressure. It could not be obtained crystalline, and gives no coloration with ferric chloride. Alcohol must not be employed in the preparation of this substance, as it decomposes the sodium compound at a high temperature. The fact that the ethyl compound is volatile without decomposition, whilst the unalkylated compound decomposes on heating with formation of an α-pyrone derivative, is in full accordance with the explanation already given by the authors of the latter reaction (*loc. cit.*).

On hydrolysis, ethyl ethyldicarboxyglutaconate is converted into *ethylglutaconic acid*, $COOH \cdot CHEt \cdot CH\vdots CH \cdot COOH$, which is a white, crystalline compound melting at 118—120°. Its *silver* salt is a white precipitate, and fairly stable towards light.

Ethyl benzyldicarboxyglutaconate,

$$C(COOEt)_2(CH_2Ph) \cdot CH\vdots C(COOEt)_2,$$

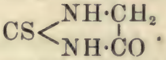
is prepared in the manner described by Conrad and Guthzeit (*Annalen*, **222**, 258), and is also volatile without decomposition, boiling at 240° (uncorr.) under 11—12 mm. pressure; it crystallises from alcohol in glassy, rectangular crystals melting at 78°. It is very slowly reduced by zinc-dust and acetic acid.

The ethyl compound, on the other hand, is readily reduced by these reagents with formation of *ethyl ethyldicarboxyglutarate*, $CEt(COOEt)_2 \cdot CH_2 \cdot CH(COOEt)_2$, which is also an oil boiling at 195—197° (uncorr.) under 10—11 mm. pressure. On treatment with sodium ethoxide and benzyl chloride, it is converted into *ethyl ethylbenzyldicarboxyglutarate*, $(COOEt)_2CEt \cdot CH_2 \cdot C(CH_2Ph)(COOEt)_2$, which is an extremely thick oil boiling at 210—230° under 12 mm. pressure. On hydrolysis, it yields a syrupy tetracarboxylic acid which slowly becomes crystalline, and loses carbonic anhydride on heating at 100—210°; a syrup then remains which on analysis gave numbers approximately agreeing with those required by *ethylbenzylglutaric acid*, $COOH \cdot CHEt \cdot CH_2 \cdot CH(CH_2Ph) \cdot COOH$. It has not yet been obtained pure or crystalline, but the neutral solution of its ammonium salt yields more or less insoluble precipitates with salts of most of the heavy metals.

H. G. C.

Thiocarbimidoacetic Acid and Thiohydantoïn. By P. KLASON (*Chem. Centr.*, 1890, ii, 344; from *Ofv. Köngl. Vet. Akad.*, 1890, 87).—The author considers that Claus and Neuhöffer's reaction of ethyl bromide on thiohydantoïn is explained thus:—The ethyl bromide reacts with the alcohol with formation of hydrogen bromide, which then reacts with the thiohydantoïn with formation of ammonia and thiocarbimidoacetic acid, the latter becoming further converted into thioglycollic acid, carbonic anhydride, and ammonia. *Ethyl thiocarbimidoacetate*, $CSN{\cdot}CH_2{\cdot}COOEt$, is formed by the action of carbon thiochloride on ethyl amidoacetate. The carbon thiochloride is diluted with ether, and the ethyl amidoacetate added drop by drop, the mixture being kept cool; ether is then added, filtered from the ethyl amidoacetate hydrochloride, the filtrate distilled, the impure ethyl thiocarbimidoacetate distilled with steam, extracted from the water with ether, and finally distilled in a vacuum. It is thus obtained as a colourless, somewhat thick liquid, having a feeble odour of oil of mustard, boiling at 110° under a pressure of 12 mm. Sp. gr. = 1·1649 at 18°/4°.

Thiohydantoïn is obtained by heating a mixture of ethyl amidoacetate hydrochloride and dry potassium thiocyanate in molecular proportion at 140—150°. The mass is dissolved in water, hydrochloric acid added, and the solution evaporated. The compound has the formula



$$CS<\begin{matrix}NH{\cdot}CH_2\\ |\\ NH{\cdot}CO\end{matrix}$$

. When heated with barium hydroxide, *thiohydantoic acid*, $C_3H_6N_2SO_2$, is formed, which crystallises in beautiful, colourless prisms, very slightly soluble in cold water. Mercuric oxide converts it into hydantoic acid. Ethyl hydantoate is formed in like manner to thiohydantoïn if potassium cyanate is substituted for the thiocyanate, and forms beautiful prisms somewhat readily soluble in hot water, and melting at 138·5°. J. W. L.

Hydrolysis of Sulphones. By E. Stuffer (*Ber.*, **23**, 3226—3241; compare Abstr., 1890, 987).—*Diisopropylsulphonediethylmethane*, $CEt_2(SO_2Pr^{\beta})_2$, is formed in small quantities, the principal product being potassium isopropylsulphonate, when the condensation product of diethyl ketone and isopropyl mercaptan is oxidised with potassium permanganate and dilute sulphuric acid. It crystallises from hot water in small plates, melts at 97°, and is insoluble in cold water and alcohol, but readily soluble in ether, chloroform, benzene, and hot alcohol. Like diethylsulphonedimethylmethane (sulphonal), it is not hydrolysed by boiling 30 per cent. aqueous or alcoholic potash.

Potassium isopropylsulphonate, $C_3H_7SO_3K$, crystallises from hot alcohol in plates, and is readily soluble in water.

Diisobutylsulphonedimethylmethane, $CMe_2(SO_2{\cdot}CH_2Pr^{\beta})_2$, prepared by oxidising the condensation product of acetone and isobutyl mercaptan, forms colourless crystals, melts at 64°, and is only sparingly soluble in hot water, but moderately easily in alcohol, and readily in chloroform, carbon bisulphide, benzene, and ether; it is not hydrolysed by boiling aqueous or alcoholic potash. The yield of the sulphone is only small, as the principal product of the reaction is the potassium salt of the sulphonic acid.

Diisoamylsulphonedimethylmethane, $CMe_2(SO_2{\cdot}CH_2{\cdot}CH_2Pr^{\beta})_2$, obtained in like manner from isoamyl mercaptan, forms crystalline scales, melts at 72°, and resembles the preceding compound in its behaviour with solvents and alkalis.

Diethylsulphonemethane (compare Fromm, Abstr., 1890, 55) is not acted on by boiling alcoholic or aqueous potash or by sodium ethoxide in boiling alcoholic solution, but when heated with sodium ethoxide at a temperature above 100°, it is completely decomposed.

Diisobutylsulphonemethane, $CH_2(SO_2{\cdot}CH_2Pr^\beta)_2$, prepared by oxidising the condensation product of formaldehyde and isobutyl mercaptan, forms colourless crystals, melts at 85°, and is soluble in alcohol, ether, chloroform, benzene, and hot water, but insoluble in cold water; it resembles diethylsulphonemethane in its behaviour with alkalis. The *dibromo*-derivative, $CBr_2(SO_2{\cdot}CH_2Pr^\beta)_2$, is a crystalline compound melting at 77—78°.

Propylene diethyl sulphide is obtained when propylene bromide is treated with ethyl mercaptan and sodium ethoxide; it is a mobile oil, cannot be distilled, and is decomposed by oxidising agents, but without yielding propylenediethylsulphone.

Propylene diphenyl sulphide can be prepared by boiling phenyl mercaptan with propylene bromide and 10 per cent. soda for a few hours; it is a heavy oil and cannot be distilled.

Propylenediphenylsulphone, $C_3H_6(SO_2Ph)_2$, is formed by oxidising the sulphide with potassium permanganate; it forms colourless, lustrous plates, melts at 113°, and is soluble in hot alcohol, benzene, chloroform, and hot water, but only sparingly soluble or insoluble in ether and carbon bisulphide, and insoluble in cold water. When boiled with dilute potash, it is decomposed into benzenesulphinic acid and a colourless oil which is probably phenylsulphonepropyl or phenylsulphoneisopropyl alcohol.

Trimethylenediethylsulphone, $C_3H_6(SO_2Et)_2$, can be easily prepared by oxidising trimethylene diethyl sulphide, the condensation product of trimethylene bromide and ethyl mercaptan, with potassium permanganate and dilute sulphuric acid. It crystallises in colourless plates or needles, melts at 183°, and is readily soluble in hot water, but only sparingly in ether, chloroform, benzene, cold alcohol, and cold water; it is not decomposed by hot soda, in which it is soluble, and it is very stable towards bromine and oxidising agents.

Trimethylenediphenylsulphone, $C_3H_6(SO_2Ph)_2$, obtained by heating trimethylene bromide with sodium benzenesulphinate in alcoholic solution, separates from dilute alcohol in crystals, melts at 125—126°, and is almost insoluble in water and cold alcohol, but moderately easily soluble in hot alcohol, benzene, and ether, and very readily in chloroform. It is not acted on by boiling soda or by oxidising agents.

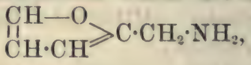
A *trisulphone* of the constitution $SO_2Et{\cdot}CH_2{\cdot}CMe(SO_2Et)_2$ is obtained when chloracetone is heated with ethyl mercaptan and concentrated hydrochloric acid, and the light-yellow oily product oxidised with potassium permanganate and sulphuric acid. It crystallises from hot water in needles, melts at 137°, and is readily soluble in hot alcohol; it is completely decomposed by warm soda, yielding ethylsulphinic acid.

F. S. K.

Action of Acid Chlorides on Bases in presence of Alkali.

By W. MARCKWALD (*Ber.*, **23**, 3207—3208).—It has already been pointed out by Hinsberg (this vol., p. 49) that the reaction employed by Schatten and Baumann for the preparation of benzoyl derivatives is of very general application. The author has found that a benzene solution of carbonyl chloride also acts in a similar manner on organic bases in presence of an excess of alkali, thus forming a ready method of preparing symmetrically substituted carbamides; the urethanes may also be prepared in a similar manner from the alkyl chloroformates.

In addition to the substituted carbamides which are known, the following derivatives of furylamine,



$\begin{matrix}\mathrm{CH{-}O}\\ \| \\ \mathrm{CH{\cdot}CH}\end{matrix}\!\!>\!\mathrm{C{\cdot}CH_2{\cdot}NH_2}$, have been prepared.

Symmetrical Difurylcarbamide, $CO(NH\cdot CH_2\cdot C_4H_3O)_2$.—To obtain this compound, a mixture of furylamine with aqueous caustic potash is shaken with a slight excess of a benzene solution of carbonyl chloride until the odour of the latter has disappeared, part of the carbamide separating out. The benzene is evaporated, the separated difurylcarbamide collected, and recrystallised from benzene. It forms small, nacreous plates which are sparingly soluble in all the ordinary solvents, melts at 128°, and has an intense odour resembling that of the dwarf plume-thistle (*Carlina acaulis*).

Ethyl furylcarbamate, $C_4H_3O\cdot CH_2\cdot NHCOOEt$, is obtained in a corresponding manner from furylamine and ethyl chloroformate. It is extracted from the aqueous solution with ether, and remains, after distilling off the latter, as a yellowish oil which has a pleasant odour. On heating, it distils at 240°, forming a colourless liquid, which has, however, then an unpleasant odour, probably owing to the formation of traces of furylcarbamine. H. G. C.

Rationale of Reactions in the presence of Aluminium Chloride and Bromide. By G. GUSTAVSON (*J. pr. Chem.* [2], **42**, 501—507). —Friedel and Crafts (Abstr., 1889, 241) attributed the action of aluminium chloride and bromide in facilitating the displacement of the hydrogen in benzene, &c., to the formation of such compounds as $C_6H_5\cdot Al_2Cl_5$, which, however, could only be isolated in the absence of hydrochloric acid, for this decomposes them. If such be the case, the author asserts that such a compound as $C_6H_5SO_2\cdot Al_2Cl_5$ should also exist, for aluminium chloride brings about a reaction between sulphurous anhydride and benzene (*loc. cit.*); but there is no evidence that such a compound is formed when sulphurous anhydride is passed into a mixture of benzene and aluminium chloride; indeed, according to Adrianowsky (Abstr., 1879, 915), quite a different reaction takes place.

Friedel and Crafts fail to see how the compounds $AlCl_3(C_6H_6)_3$, &c., which are formed according to the author's theory (Abstr., 1885, 363), and are exothermic, can facilitate substitution; the author replies that it is equally difficult to explain how hydrogen which has combined with nitrogen in the exothermic compound ammonia should be more ready to react with methyl chloride, &c., than when in the free state. The author has obtained and analysed the compound $AlCl_3,3C_7H_8$; such compounds as this are decomposed by heat, and will not explain those reactions which only take place at high temperatures. A. G. B.

Meta- and Para-ethylisopropylbenzene. By P. v. d. Becke (*Ber.*, **23**, 3191—3196).—The preparation of these hydrocarbons may be readily carried out by means of Friedel and Crafts' reaction. It has been shown by Gustavson (*Ber.*, **11**, 1251), Silva (Abstr., 1885, 1054), and Kekulé and Schrötter, that in the presence of aluminium chloride the propyl group is converted into isopropyl, and in preparing the above hydrocarbon it is immaterial whether propyl or isopropyl bromide is employed. 300 grams of ethylbenzene were therefore mixed with 50 grams of aluminium chloride, and 450 grams of propyl bromide gradually added. After remaining for eight days, the product is washed, dried, and fractionated; the fractions 189—195° and 195—201° contain the meta- and para-ethylisopropylbenzene respectively. The fraction 150—155° is isopropylbenzene, the properties of which agree with the statements of Claus and Tonn (Abstr., 1885, 903), except that the author finds the melting point of the sulphonamide to be 93—94° instead of 127°. The fraction 179—185° contains diethylbenzenes, and that boiling at 204—208° consists probably of di-isopropylbenzenes.

To obtain the pure hydrocarbons from the fractions boiling at 189—195° and at 195—201° respectively, both are sulphonated with a mixture of 1 vol. of concentrated sulphuric acid and $\frac{1}{2}$ vol. of fuming acid, the first sulphonic acid being isolated as the barium salt, and the second as the magnesium salt. These are then converted into the potassium salts, and the latter heated with hydrochloric acid under pressure.

Metethylisopropylbenzene is a colourless, pleasant-smelling liquid, which boils at 190—192°, does not solidify at −20°, and on oxidation yields isophthalic acid. *Barium metethylisopropylbenzenesulphonate* crystallises in anhydrous, fascicular aggregates of needles, sparingly soluble in water, whilst the *copper* salt crystallises with 4 mols. H_2O in blue plates which have a satin-like lustre. The *sulphochloride* and *sulphonamide* are oils.

Parethylisopropylbenzene is a liquid which is more strongly refractive than water, boils at 197—198°, and does not become solid at −20°. On oxidation, it is converted into terephthalic acid. *Magnesium parethylisopropylbenzenesulphonate* crystallises with 4 mols. H_2O in tablets which are sparingly soluble in water. The *copper* salt also crystallises with 4 mols. H_2O, and forms blue, satiny plates; whilst the *potassium* salt could only be obtained as an amorphous, readily soluble mass. The *sulphochloride* is an oil, and the *sulphonamide* only becomes partially solid in the exsiccator. The *sulphonanilide*, on the other hand, crystallises in nodular aggregates of prisms melting at 92—93°.

Nitroparethylisopropylbenzene is obtained by the nitration of the hydrocarbon in acetic acid solution, and forms a yellowish-brown oil which boils at 265° with partial decomposition. On treatment with zinc and acetic acid, it is slowly reduced to *amidoparethylisopropylbenzene*, the hydrochloride of which forms fascicular aggregates of needles, becoming brown in the air. *Parethylisopropylphenol* is obtained by fusing the potassium sulphonate with caustic potash, and is a yellow oil boiling at 228—230°, almost insoluble in water, but readily soluble in alcohol and ether.

The author has also prepared *parethylpropylbenzene* according to Sempotowski's method (Abstr., 1890, 54). It boils at 199—200°, and yields, on sulphonation, only one *sulphonic acid*, the *magnesium* salt of which crystallises in small prisms containing 4 mols. H_2O. and is readily soluble in water. The *sulphonamide* crystallises from dilute alcohol in small plates which melt at 84°, and the *sulphonanilide* in fascicular aggregates of slender needles melting at 97—98°.

H. G. C.

Diisopropylbenzene. By E. UHLHORN (*Ber.*, **23**, 3142—3144).—A mixture of two hydrocarbons, boiling at 200—210°, is obtained in the preparation of isopropylbenzene (b. p. 153°) by Friedel and Craft's method; the two compounds can be separated from one another by shaking the mixture with concentrated sulphuric acid, converting the sulphonic acids thus produced into their copper or barium salts, and separating the salts by fractional crystallisation.

Barium metadiisopropylbenzenesulphonate crystallises in long needles with 2 mols. H_2O, and is only sparingly soluble in water. The *copper* salt, with 4½ mols. H_2O, forms long, bluish needles, and is readily soluble. The *magnesium* salt, with 4 mols. H_2O, crystallises in well-defined, prismatic plates, and is rather sparingly soluble in water. The sodium and the calcium salts crystallise in needles, and are very readily soluble in water.

Metadiisopropylbenzenesulphonamide crystallises in colourless plates, and melts at 145°.

Trinitrometadiisopropylbenzene forms yellowish needles, and melts at 110—111°. *Metadiisopropylbenzene*, prepared by heating the sulphonamide with hydrochloric acid at 180°, boils at 204°, and, on oxidation with dilute nitric acid, is converted into isophthalic acid.

Copper orthodiisopropylbenzenesulphonate crystallises in plates with 6½ mols. H_2O, and is sparingly soluble in water. The magnesium, calcium, and sodium salts are very readily soluble. The *sulphonamide* melts at 102°, and yields *orthodiisopropylbenzene* boiling at 209°, which, on oxidation, is converted into phthalic acid. F. S. K.

Nononaphthene and its Derivatives. By I. KONOVALOFF (*J. Russ. Chem. Soc.*, **22**, 4—23 and 118—148).—Several years ago, Markovnikoff and Ogloblin obtained from Caucasian petroleum a series of hydrocarbons, "*naphthenes*," of the general formula C_nH_{2n}, having the properties of saturated compounds of the aromatic series. Nononaphthene was obtained from Balachana and Bibi-Eibat petroleum by treating the fraction boiling between 125—140° with fuming sulphuric acid at 40°, washing with aqueous soda and water, drying, and rectifying over sodium, and, after repeated fractional distillation, again purifying it in the same manner. The fraction boiling at 135—136° consists of the hydrocarbon *nononaphthene*, C_9H_{18}; its sp. gr., when prepared from the first-named source, is 0·7664 (20/20°), from the second 0·7647. As sulphuric acid acts on nononaphthene, it is not without reason that

Mendeléeff recommended that the use of this reagent for its purification should be avoided. With excess of sulphuric acid, nononaphthene gives pseudocumenesulphonic acids. Sulphur or antimony pentachloride at high temperatures gives indefinite mixtures of thio- or chloro-derivatives. By the action of bromine and aluminium bromide, part of the hydrocarbon is converted into tribromopseudocumene. Nitric acid of sp. gr. 1·4 is without action in the cold, but if the hydrocarbon is heated at 120—130°, with the same acid diluted with two volumes of water, nitro-derivatives are obtained such as $C_8H_{15}NO_2$; this boils at 218—220°, and on treatment with hydrochloric acid and tin, an amine, $C_8H_{15}\cdot NH_2$, isomeric with coniïne is obtained. It smells like that alkaloïd, boils between 172° and 177°, and gives only in a feeble degree Hofmann's reaction for primary amines. Its sp. gr. is 0·8727 at 0°, and it is a strong base, combining with acids, and absorbing carbonic anhydride from the atmosphere.

Nononaphthene was heated with hydriodic acid with the object of hydrogenating it, but nonane was not formed. By the action of chlorine, chlorides were obtained, containing principally $C_9H_{17}Cl$, boiling at 185—187°. The chloride was converted into the iodide $C_9H_{17}I$ by heating it with strong hydriodic acid at 150—160°; this boils at 108—111° under a pressure of 200 mm. On heating the chloride or the iodide with silver acetate and acetic acid, the *acetate*, $CH_3\cdot COOC_9H_{17}$, was obtained; it boils at 208·5°. This, on hydrolysis, yields *nononaphthyl alcohol*, $C_9H_{17}\cdot OH$, boiling at 189—192°; sp. gr. = 0·8972 at 20°/20°; and the alcohol, on treatment with phosphorus pentachloride, yields the chloride $C_9H_{17}Cl$, mentioned above and having the same properties. A solution of the iodide in ether, when heated with silver oxide, yields the *ether* $(C_9H_{17})_2O$, boiling at 300·5°; sp. gr. 0·8662 at 20°/20°. The elements of hydrogen chloride are easily removed from the chloride, $C_9H_{17}Cl$, with formation of *nononaphthylene*, C_9H_{16}; this boils at 135—137°, and has sp. gr. 0·8068 at 0°. With bromine, nononaphthylene yields a dibromide, $C_9H_{16}Br_2$, which is easily split up into hydrogen bromide and the bromo-derivative $C_9H_{15}Br$, but it is impossible to saturate the compound with bromine up to the limit. Oxidation of nononaphthene and its alcohol with chromic mixture yields a complicated mixture of acids. Nononaphthene is proved to be *hexahydropseudocumene* [b. p. 135—138°; sp. gr. 0·7667 (20/0°)]. It has hitherto been found to be impossible to convert it by hydrogenation into nonane, the corresponding saturated hydrocarbon of the fatty series. B. B.

Caucasian Petroleum. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, **22**, 23—26).—By fractional distillation of the lower boiling portions of Caucasian petroleum, previously purified by fuming sulphuric acid, the author has obtained a series of fractions boiling between 32° and 72°, and not further separable by fractional distillation. The relation between the boiling points and the densities shows that the higher fractions contain a comparably larger proportion of naphthenes having a higher density than the corresponding paraffins, whereas the latter are more abundant in the fractions of lower boiling point. It is shown that the portion boiling between 57° and 60° contains neither hexanaphthene nor benzene, and that it consists principally of dipseudopropyl C_6H_{14}. The fraction 45—48° contains hexane (trimethylethylmethane) and pentane; the fraction 32—36° consists chiefly of dimethylethylmethane, whilst the fraction boiling above 60° contains normal hexane. B. B.

Action of Thionyl Chloride on the Phenols. By G. TASSINARI (*Gazzetta*, **20**, 362—366).—The action of thionyl chloride on the phenols results in the formation of a mixture of variable quantities of three substances, namely (1), a compound of high melting point not examined further; (2) a dihydroxythiobenzene identical with that obtained by the action of sulphur dichloride on phenol (Abstr., 1889, 245); (3) chlorinated and sulphuretted resins. Hydrogen chloride and sulphurous anhydride are also evolved during the reaction. Thionyl chloride has a similar action on orthocresol and thymol, the only difference being that with orthocresol a good deal of the compound of high melting point is formed, and but little of the dihydroxythiobenzene, the reverse occurring with thymol; paracresol is scarcely affected in the cold, only a trifling quantity of liquid chloroparacresol being formed.

The dihydroxythiobenzene previously described (*loc. cit.*) has the following crystallographic characters. The crystals belong to the monoclinic system:—$a : b : c = 0{\cdot}41564 : 1 : 0{\cdot}26415$; $\beta = 86° 48'$. The derived hydroxysulphonebenzide crystallises in the rhombic system:—$a : b : c = 0{\cdot}78133 : 1 : 0{\cdot}415568$; $\beta = 90°$. S. B. A. A.

Condensation Products of Glyoxal and some Mercaptans. By E. STUFFER (*Ber.*, **23**, 3241—3245).—Glyoxal combines with ethyl mercaptan in presence of hydrochloric acid, but the product cannot be obtained in a pure condition, nor can it be converted into a tetrasulphone by oxidation with potassium permanganate.

Tetrathiophenylglyoxal, $CH(SPh)_2{\cdot}CH(SPh)_2$, is formed when glyoxal sodium hydrogen sulphite is warmed with phenyl mercaptan in alcoholic hydrochloric acid solution. It separates from alcoholic chloroform as a colourless powder, melts at 115°, and is very readily soluble in chloroform, but only sparingly in boiling alcohol, and insoluble in water and alkalis. It dissolves in warm concentrated sulphuric acid with a cherry-red coloration, is readily oxidised and decomposed by concentrated nitric acid, and combines with bromine, yielding a yellow, oily compound; when treated with potassium permanganate under various conditions, it is either unchanged or completely decomposed, so that the corresponding sulphone cannot be obtained. F. S. K.

Nitrometacresols. By W. STAEDEL and A. KOLB (*Annalen*, **259**, 208—227; compare Abstr., 1889, 497).—The two metanitrocresols which are obtained by nitrating pure cresol, prepared from thymol, can be easily separated by distillation with steam. The non-volatile compound (m. p. 129°) crystallises from water and alcohol in needles, is very readily soluble in benzene, ether, chloroform, alcohol, and hot water, and dissolves in alkaline carbonates with evolution of carbonic anhydride. The *ammonium* derivative forms long, yellow needles, and the *silver* derivative is a yellowish-red compound almost insoluble in water. The *potassium* derivative, $C_7H_6NO_3K + 2H_2O$, and the *sodium* derivative, with $2H_2O$, crystallise in yellow plates, and the *barium* derivative in silky needles. The ethyl derivative melts at 53—54°, and is identical with the compound obtained by nitrating metacresol ethyl ether.

Orthonitrometatoluidine [$Me : NH_2 : NO_2 = 1 : 3 : 6$], prepared by heating nitrometacresol ethyl ether with concentrated ammonia at 140—150°, crystallises from water in slender, yellow needles, melts at 134°, and is readily soluble in alcohol, ether, and hot water; when treated with sulphuric acid and sodium nitrite in alcoholic solution, it is converted into nitrotoluene (b. p. 220—221°).

Amidometacresol [$Me : OH : NH_2 = 1 : 3 : 6$], obtained by reducing the nitro-compound with tin and hydrochloric acid, is a grey powder melting at 174° with decomposition. The *hydrochloride*, C_7H_9ON,HCl, crystallises in colourless plates. The *acetyl* derivative, $C_9H_{11}NO_2$, crystallises from water, in which it is readily soluble, in colourless plates containing 1 mol. H_2O; these melt at 80° and lose their water at 110—120°; the anhydrous compound melts at 125°, and is sparingly soluble in benzene.

Methylquinonechlorimide, C_7H_6NOCl, is precipitated when a concentrated solution of calcium hypochlorite is added to a dilute aqueous solution of amidometacresol hydrochloride. It crystallises from alcohol in golden prisms, melts at 75°, and explodes at a higher temperature.

Dinitrometacresol ethyl ether [$Me : OEt : (NO_2)_2 = 1 : 3 : 4 : 6$] is formed when the corresponding mononitro-compound is treated with fuming nitric acid. It crystallises from dilute alcohol in colourless needles, and melts at 97°.

Dinitrometatoluidine, prepared by heating the preceding compound with ammonia at 100°, separates from xylene in yellow crystals, melts at 195°, and is only sparingly soluble in alcohol and benzene; when treated with nitrous acid under suitable conditions, it is converted into α-dinitrotoluene [$Me : (NO_2)_2 = 1 : 4 : 6$].

Trinitrometacresol ethyl ether [$Me : (NO_2)_3 : OEt = 1 : 2 : 4 : 6 : 3$] crystallises from alcohol in slender needles or in thick prisms melting at 75°; it is probably identical with the compound (m. p. 72°) obtained by Nölting and von Salis from the silver derivative of trinitrocresol; when treated with alcoholic ammonia, it is converted into trinitrotoluidine (m. p. 136°).

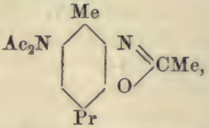
The volatile nitrometacresol (m. p. 56°) crystallises from ether in yellow plates, and is only very sparingly soluble in water, but very readily in alcohol, ether, benzene, and chloroform. The *potassium* derivative crystallises in red needles, and is very readily soluble in water. The *ethyl* derivative, $C_9H_{11}NO_3$, crystallises from alcohol in colourless needles, melts at 50—51°, and is very readily soluble in most of the ordinary solvents.

Nitrometatoluidine [$Me : NH_2 : NO_2 = 1 : 3 : 4$], prepared by heating the ethyl derivative with ammonia at 140—150°, crystallises from water in golden plates, melts at 109°, and is moderately easily soluble in alcohol, ether, benzene, chloroform, and hot water; ethyl nitrite at 100° converts it into paranitrotoluene.

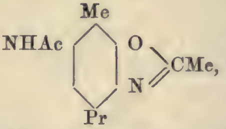
When nitrometacresol ethyl ether (m. p. 50—51°) is treated with nitric acid, it is converted into a dinitro-compound identical with that (m. p. 97°) obtained from the isomeride described above.

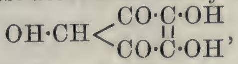
F. S. K.

Constitution of Thymol and Carvacrol Derivatives. By G. Mazzara (*Gazzetta*, **20**, 417—427).—*Tetracetyldiamidothymol acetate* [Me : NAc_2 : OAc : Pr : NAc_2 = 1 : 2 : 3 : 4 : 6], prepared by heating diamidothymol hydrochloride with acetic anhydride, crystallises from dilute alcohol in shining, white scales, softens at 179°, and melts at 184—186°. It is insoluble in alkalis.

Diacetylamidoethenylamidothymol,  is obtained as a bye-product in the preparation of the preceding compound. It is prepared by heating that compound or its constituents at a temperature of 200° to 260°. It crystallises from light petroleum in large, colourless, transparent, rhombohedric tables, melts at 92—94°, and dissolves in the ordinary solvents. It is decomposed by prolonged digestion with alkalis yielding products which impart a violet coloration to the liquid. The action of dilute hydrochloric acid removes one acetyl group from this compound, leaving *monacetylamidoethenylamidothymol*, a substance which crystallises from alcohol in yellowish or violet needles melting at 132—134°. It dissolves readily in alcohol and benzene. It is reconverted into the diacetyl derivative by heating with acetic anhydride at 200°. It is decomposed by digestion with alkalis or acids.

The action of acetic anhydride on diamidothymol hydrochloride at 160° results in the formation of a mixture of *di-*, *tri-*, and *tetracetyldiamidothymol*. These compounds are all soluble in potash, forming pink solutions, from which acids precipitate the diacetyl derivative. They also dissolve in boiling water and in dilute alcohol, crystallising out in white or pale-violet scales. The tetracetyl compound melts at 216—222°, the triacetyl compound at 238—240°, and the diacetyl derivative at 260—262°.

Acetylamidoethenylamidocarvacrol,  prepared by heating diamidocarvacrol hydrochloride with excess of acetic anhydride at 210°, crystallises from alcohol in yellowish needles and melts at 190—192°. The formation of this ethenyl derivative and of the benzenyl derivative previously described (this vol. p. 48) support the author's view, that in dinitrocarvacrol the two nitroxyl groups are in the meta-position relatively to each other. S. B. A. A.

Constitution of Rhodizonic Acid. By R. NIETZKI (*Ber.*, **23**, 3136—3141).—The author agrees with Nef (Abstr., 1890, 1270) that rhodizonic acid has the constitution $C_6O_4(OH)_2$ [$O_4 : (OH)_2 = 1:2:3:4:5:6$], and not the symmetrical constitution [$O_4 : (OH)_2 = 1:2:4:5:3:6$]. One of the principal facts which points to this conclusion is that croconic acid hydride, $C_5H_4O_5$, a compound which is formed from rhodizonic acid under the influence of concentrated alkalis, does not combine with orthodiamines, whereas croconic acid, $C_5H_2O_5$, is readily converted into azines. This difference in behaviour is best accounted for by assuming that the hydride has the constitution  $OH{\cdot}CH{<}\begin{array}{l}CO{\cdot}C{\cdot}OH\\ \quad\;\;\,\|\\ CO{\cdot}C{\cdot}OH\end{array}$, and the formation of a compound of this nature from rhodizonic acid can only be explained by assuming that the latter has the asymmetrical structure. The existence of dinitrosoresorcinoltetroxime, $C_6H_2(N{\cdot}OH)_4$ [$(NOH)_4 = 1:2:3:4$], seems to show that the quinone of the constitution $C_6H_2O_4$ [$O_4 = 1:2:3:4$] is also capable of formation, whereas no symmetrical paradiquinone has yet been obtained; this argument, as well as the behaviour of rhodizonic acid with orthodiamines, bears out the author's views regarding the constitution of rhodizonic acid. F. S. K.

Replacement of the Hydrogen Atoms in the Methylene Group. By O. WALLACH (*Annalen*, **259**, 300—309).—The hydrogen atoms of a methylene group which is in direct combination with basic radicles are readily displaced by negative elements, more especially by sulphur; and in most cases, the reaction proceeds so well that it can be conveniently employed for the preparation of various sulphur compounds.

When benzylaniline (1 mol.) is heated with sulphur (2 atoms) at 220° until the evolution of hydrogen sulphide ceases, thiobenzanilide is formed; if, however, the temperature is raised to 250—260°, and the heating is continued, benzenylamidothiophenol (m. p. 115°) is obtained. Benzyltoluidine and other benzyl bases behave like benzylaniline.

Tetramethyldiamidothiobenzophenone can be easily obtained by heating tetramethyldiamidophenylmethane (50 grams) with sulphur (15 grams) at 230° until the evolution of hydrogen sulphide is at an end; thiobenzamide can be prepared by heating benzylamine with sulphur at 180°.

Tribenzylamine combines with bromine in glacial acetic acid solution, yielding a compound of the composition $(C_7H_7)_3NBr_2$; this substance crystallises in golden needles, melts at 157—159°, is reconverted into tribenzylamine by sulphurous acid, and when boiled with water, is decomposed into benzaldehyde, dibenzylamine, and tribenzylamine.

When benzylamine is treated with bromine in glacial acetic acid solution, it yields a crystalline substance melting at 103°, which seems to have the composition $CH_2Ph{\cdot}NH_2Br_2$; this bromo-compound is decomposed by warm water and alcohol, and also on exposure to the air, into benzonitrile and benzylamine hydrobromide. F. S. K.

Action of Paratoluidine and Aniline on Phloroglucinol. By G. Minunni (*Gazzetta*, **20**, 319—355).—Phloroglucinol reacts very energetically with paratoluidine or aniline forming compounds analogous to those obtained by the action of the aromatic amines on monhydric and dihydric phenols. Both symmetrical triparatolyltriamidobenzene, $C_6H_3(NH\cdot C_7H_7)_3$, the product of the action of paratoluidine on phloroglucinol, and triphenyltriamidobenzene, obtained from aniline and phloroglucinol, together with a number of their derivatives, have already been described (Abstr., 1888, 1081). The following are additional products:—The *nitrosyl* derivative of triparatolyltriamidobenzene, $C_6H_3[N(C_7H_7)\cdot NO]_3$, crystallises from boiling alcohol in slender, deep-brown needles, melts at 233—234°, and dissolves sparingly in hot benzene and in alcohol after prolonged boiling; it is readily soluble in concentrated sulphuric acid forming a dirty-green solution.

Diparatolyldiamidohydroxybenzene, $OH\cdot C_6H_3(NH\cdot C_7H_7)_2$, prepared by heating a mixture of phloroglucinol (1 mol.) and paratoluidine (2 mols.) for six hours at 140—150°, crystallises when pure from a mixture of ether and light petroleum in colourless needles, melts at 120—121°, and, on exposure to the air, turns grey at first, but becomes intensely brown after a time. It dissolves readily in cold benzene, alcohol, and ether, and in hot alkalis, but only very sparingly in boiling water and in concentrated hydrochloric acid. It is also soluble in concentrated sulphuric acid forming a colourless solution which turns brown on heating, and reddish on addition of a little potassium nitrite. The *hydrochloride* may be obtained as a yellow, flocculent, amorphous precipitate which decomposes as soon as it is removed from the acid solution. The *platinum salt*,

$$OH\cdot C_6H_3(NHC_7H_7)_2,PtCl_4,$$

crystallises in brilliant, bronze-coloured scales, insoluble in ether, and only very sparingly soluble in boiling alcohol; it is decomposed by hot water; on heating to 260°, it is converted into a brown, amorphous powder.

The *acetyl* derivative, $OH\cdot C_6H_3(NAcC_7H_7)_2$, crystallises in colourless, microscopic prisms, melts at 128—129°, and dissolves in cold alcohol and benzene, and very sparingly in ether. It is also sparingly soluble in alkalis, and more readily in concentrated acids. Ammonia precipitates it unchanged from its hydrochloric acid solution.

The *benzoyl* derivative, $OBz\cdot C_6H_3(NBzC_7H_7)_2$ (?), forms a colourless, crystalline powder consisting of microscopic plates, and melts at 262—264°. It is almost insoluble in ether, and only very sparingly soluble in alcohol and benzene. It is insoluble in alkalis, but dissolves in concentrated sulphuric acid, and is reprecipitated unchanged on diluting the solution. Its composition is doubtful.

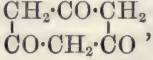
The *nitrosyl* derivative, $OH\cdot C_6H_3(NC_7H_7\cdot NO)_2$, crystallises in brownish-red, microscopic needles which darken on heating to 230°, but do not fuse even at 260°. It is very sparingly soluble in alcohol and benzene, and almost insoluble in ether.

The *nitrosyl* derivative of triphenyltriamidobenzene, $C_6H_3(NPh\cdot NO)_3$, crystallises from alcohol in brilliant, brown needles, melts at 264—265°, and is almost insoluble in alcohol and benzene. It dissolves in cold concentrated sulphuric acid forming a solution which appears dark-green by reflected light, and copper-coloured in the magnesium light.

Diphenyldiamidohydroxybenzene, $OH\cdot C_6H_3(NHPh)_2$, is prepared by heating phloroglucinol with aniline in the theoretical proportions for six hours at 140—150°. It crystallises from a mixture of ether and petroleum in slender, white needles which acquire a grey tinge after some time, melts at 94—95°, and dissolves readily in cold alcohol, benzene, and ether, but only sparingly in water, alkalis, and hydrochloric acid. On cooling its solution in potash, a substance separates out, readily soluble in water. It dissolves in cold concentrated sulphuric acid, and the solution turns blue on the addition of a little sodium nitrite, and brownish-red when a larger quantity is added. The *hydrochloride*, $OH\cdot C_6H_3(NHPh)_2,2HCl$, is an amorphous, brownish-yellow powder which is decomposed by hot water; it melts at 85—90°, and is soluble in alcohol, but not in ether. The *platinum salt*, $OH\cdot C_6H_3(NHPh)_2,PtCl_4$, crystallises in large, yellowish-brown plates which darken at 230°; it dissolves readily in boiling alcohol, but is insoluble in ether. It is decomposed by boiling water.

The *acetyl* derivative, $OH\cdot C_6H_3(NPhAc)_2$, forms a white, crystalline powder which melts at 149—150°, and dissolves readily in boiling alcohol and benzene. It is moderately soluble in hot alkalis and in cold concentrated acids. Ammonia precipitates from its hydrochloric solution a white powder soluble in excess. The *benzoyl* derivative, $OH\cdot C_6H_3(NPhBz)_2$, is obtained by treating the base with benzoic anhydride. It crystallises from alcohol in large, bright-yellow needles, melts at 184—185°, and dissolves readily in the ordinary solvents, and also in boiling alkaline solutions and in cold concentrated sulphuric acid. The *nitrosyl* derivative, $OH\cdot C_6H_3(NPh\cdot NO)_2$, crystallises from boiling glacial acetic acid in bright-red needles, and blackens without melting at 250°; it is almost insoluble in the ordinary solvents, but dissolves in cold concentrated sulphuric acid. Attempts were made to prepare a dihydroxy-derivative,

$$C_6H_3(OH)_2\cdot NH\cdot C_7H_7,$$

by moderating the reaction between phloroglucinol and paratoluidine, but without success, the monhydroxy-derivative being formed in every instance; a similar failure attended an attempt to prepare mixed derivatives of the type $C_6H_3(NH\cdot C_7H_7)_2\cdot NHPh$. From the foregoing results, it appears that phloroglucinol, a trihydric phenol, reacts more energetically with aromatic amines than the dihydric phenols, which in turn are more active than the monhydric compounds. The energy of reaction must, therefore, depend directly on the number of OH-groups present. Moreover, in view of the complete analogy between the action of ammonia and that of the substituted amines, it seems probable that phloramine, the product of the action of ammonia on phloroglucinol, is also a derivative of trihydroxybenzene, and not of the secondary phloroglucinol,  $\begin{array}{c} CH_2\cdot CO\cdot CH_2 \\ | \qquad\qquad | \\ CO\cdot CH_2\cdot CO \end{array}$, as indicated by Baeyer (Abstr., 1886, 350).

S. B. A. A.

Consecutive Tetramidotoluene. By R. NIETZKI and R. RÖSEL (*Ber.*, **23**, 3216—3219).—A mixture of the mono- and di-nitro-derivatives of diacetylmetatoluylenediamine is obtained when diacetylmetatoluylenediamine is mixed with carbamide nitrate, and then gradually introduced into nitric acid (6 parts), which has been previously distilled with sulphuric acid, the temperature being kept at from 5 to 10°. The two compounds are precipitated with ice and hydrolysed with dilute sulphuric acid or dilute alkalis; the mono- and di-nitrometatoluylenediamine obtained in this way can be easily separated from one another, as the latter alone is soluble in alkalis, being reprecipitated on the addition of an acid.

Dinitrometatoluylenediamine, $C_6HMe(NO_2)_2(NH_2)_2$, forms slender, golden needles and melts above 300°.

Tetramidotoluene sulphate, $C_6HMe(NH_2)_4,H_2SO_4$, is obtained when the dinitro-compound just described, or tetrisonitrosoresorcinol [$Me : (NOH)_4 = 1 : 3 : 4 : 5 : 6$], is reduced with stannous chloride and hydrochloric acid; the filtered solution is treated with sulphuric acid, then mixed with a considerable quantity of alcohol, the precipitated sulphate dissolved in moderately dilute hydrochloric acid and reprecipitated with alcohol; it crystallises in small, almost colourless plates. When excess of sulphuric acid is added to a hydrochloric acid solution of this salt, a compound of the composition

$$C_6HMe(NH_2)_4,2H_2SO_4$$

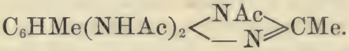
is precipitated in small plates.

Tetramidotoluene cannot be obtained by decomposing one of its salts, as it rapidly oxidises on exposure to the air; solutions of its salts are coloured brown by ferric chloride and other oxidising agents, but a definite oxidation product could not be obtained.

A *quinoxaline* of the composition $C_{35}H_{24}N_4$ is gradually deposited in yellowish-red needles when tetramidotoluene sulphate is heated with benzil and sodium acetate in alcoholic solution; it melts at 222—225°, and dissolves in concentrated sulphuric acid yielding a red solution, the colour of which changes to yellow on the addition of water.

Croconic acid also combines with tetramidotoluene, yielding a dark-brown azine, which crystallises in needles, but is so insoluble in all ordinary solvents that it cannot be purified by recrystallisation.

When tetramidotoluene sulphate is heated with sodium acetate and acetic anhydride, a compound of the composition $C_{15}H_{20}N_4O_4$ is obtained; this substance crystallises in colourless needles, melts at 305°, is moderately easily soluble in hot water, and is probably a triacetylethenyltetramidotoluene of the constitution



$$C_6HMe(NHAc)_2{<}{\overset{NAc}{\underset{N}{—}}}{\geqslant}CMe.$$

It dissolves in dilute hydrochloric acid, and on adding ammonia to the solution, a colourless, very readily soluble base melting at 282° is precipitated; judging from the analysis of the picrate, this base is probably diacetylethenyltetramidotoluene. F. S. K.

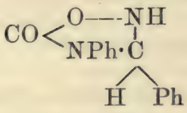
Diazo-compounds. By H. Goldschmidt (*Ber.*, **23**, 3220—3222).—The author has determined the molecular weight of meta- and para-nitrodiazobenzene nitrate and of diazobenzene chloride, in aqueous solution by Raoult's method; the experiments have shown that in very dilute aqueous solutions these salts are completely dissociated, but that in more concentrated solutions the observed molecular weight increases rather rapidly, more quickly, in fact, than is the case with most metallic salts; the electrical conductivity of solutions of diazo-salts is also being investigated. F. S. K.

Aldoximes. By E. Beckmann (*Ber.*, **23**, 3319—3331, and 3331—3341).—Salicylaldoxime (m. p. 57°) may be converted into an isomeric modification by the action of hydrochloric acid, either at the ordinary temperature or on heating. The *α-benzyl ether* of this compound is prepared by the action of sodium ethoxide and benzyl chloride, and crystallises from warm alcohol in slender, colourless, interlaced needles which melt at 62—63°.

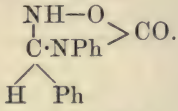
The same compound is also obtained by heating an alcoholic solution of salicylaldehyde with α-benzylhydroxylamine hydrochloride and hydrogen sodium carbonate. The corresponding *β-benzyl ether* is formed in a similar manner from β-benzylhydroxylamine, and crystallises from dilute alcohol in pale-yellow, lustrous, rectangular plates which melt at 99—100°.

Action of Phenylcarbimide on the Benzaldoximes.—The phenyl isocyanate employed in the following experiments boiled at 161—162°, and was absolutely free from hydrogen chloride. β-Benzaldoxime is dissolved in 12—14 parts of absolute ether, and treated at 5° with rather less than the calculated quantity of phenylcarbimide; a copious white precipitate is immediately formed, consisting of microscopic, quadratic plates which melt at 74—75° with evolution of gas; on boiling with dilute potash, carbonic anhydride, aniline, and diphenylcarbamide are formed. On warming equivalent quantities of β-benzaldoxime and phenylcarbimide dissolved in benzene, and evaporating the solution, crystals are deposited which melt at 94° with evolution of gas; the substance is isomeric with the previous compound, and has already been prepared by Goldschmidt (Abstr., 1890, 251). Carbonic anhydride and a trace of diphenylcarbamide are formed by the action of dilute potash. The first of these isomerides is very sparingly soluble, and is converted into the higher melting derivative on warming with benzene, but this latter cannot be transformed into the lower melting compound. Neither of the substances reacts with phenylcarbimide; with hydrogen chloride, both yield the compound (m. p. 134°) described by Goldschmidt (*loc. cit.*). By the action of dilute soda in the cold, the lower melting compound yields chiefly β-benzaldoxime, whilst benzonitrile is the principal product from the higher melting modification.

By the action of phenylcarbimide on α-benzaldoxime in ethereal solution, a compound separates which melts at 75° and is identical with the above derivative from β-benzaldoxime; if this substance is removed and the solution allowed to remain for a short time, a second compound crystallises out in needles which melt at 135°; this has previously been described by Goldschmidt. α-Benzaldoxime is, therefore, less stable than has hitherto been supposed; it is also found that by warming, or by keeping the α-aldoxime for some time, the yield of the β-derivative is increased. The author suggests that the two compounds obtained from β-benzaldoxime and phenylcarbimide are represented by the following formulæ:—



(M. p. 74°.)

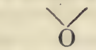
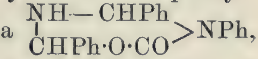


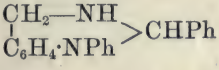
(M. p. 94°.)

Benzalbenzamide, $NHBz{\cdot}C_7H_7$, is obtained by the action of benzoic chloride on β-benzaldoxime benzyl ether, and crystallises from benzene in colourless plates which melt at 105°. Acetic chloride and phosphorus oxychloride act in a similar manner, but hydrogen chloride in benzene solution causes no change. The compound may be prepared synthetically from benzylamine and benzoic chloride. On heating the amide with hydriodic acid, benzyl iodide, benzoic acid, and ammonia are formed, whilst in similar circumstances β-benzaldoxime benzyl ether yields a small quantity of benzoic acid and benzylamine. Goldschmidt prepared a compound (m. p. 121°) by the action of phenylcarbimide on β-benzaldoxime benzyl ether; this result is confirmed. On heating with concentrated hydriodic acid, benzyl iodide is formed; boiling hydrochloric acid is without action, but on heating at 140°, complete decomposition takes place; the compound is unchanged by sulphuric acid at ordinary temperatures.

By the action of sodium ethoxide on the carbanilido-product dissolved in alcohol, carbonic anhydride is eliminated, and a basic compound of the formula $C_{20}H_{18}N_2$ is obtained, which crystallises from dilute alcohol in large, flat, rectangular plates melting at 99—100°. The *hydrochloride* crystallises with difficulty. The same compound is formed by the action of benzanilidiimido-chloride on benzylamine, and it must therefore be regarded either as symmetrical benzylphenylbenzenylamidine, or as a quinazoline derivative (see below). The compound is not acted on by hydrochloric acid and alcoholic ammonia; on heating with hydriodic acid, it yields benzoic acid, ammonia, and aniline.

On heating the carbanilido-derivative with alcoholic ammonia at 100° for an hour, benzylideneaniline is formed, together with a viscid, oily liquid which yields benzylidenephenylhydrazone on treatment with phenylhydrazine; its molecular weight is 111, as determined by Raoult's method; the compound contains two CHPh groups, together with the complex NPh, but its exact constitution is not yet determined.

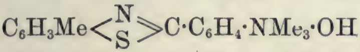
Of the three formulæ for β-benzaldoxime, namely, $PhC{:}N(OH)C_7H_7$, $OH{\cdot}CPh{:}N{\cdot}C_7H_7$, and  $\underset{\diagdown\,O\,\diagup}{PhCH{\cdot}N}{\cdot}C_7H_7$, the author has previously advanced the first two; the above results point, however, to the absence of a hydroxyl group, and consequently the third one would appear to be the most probable. The compound formed by the action of phenylcarbimide would be represented by the formula  $\left.\begin{array}{l}\mathrm{NH-CHPh}\\ \mathrm{CHPh\cdot O\cdot CO}\end{array}\right>\mathrm{NPh}$, which would account for its great stability; by the elimination of carbonic anhydride, an amidine or quinazoline derivative would be formed, with the formula $C_6H_5\cdot CH_2\cdot NH\cdot CPh{:}NPh$ or



$$\left.\begin{array}{l}\mathrm{CH_2-NH}\\ \mathrm{C_6H_4\cdot NPh}\end{array}\right>\mathrm{CHPh}$$

respectively. J. B. T.

Dyes of the Primuline Group. By E. TRAUTMANN (*Chem. Centr.*, 1890, ii, 440—441; from *Mon. Sci.* [4], **4**, 811—820).—If dehydrothiotoluidine, prepared by heating paratoluidine with sulphur (Green, Trans., 1889, 227; Gattermann and Pfitzinger, Abstr., 1889, 867), be heated with methyl alcohol and hydrogen chloride or iodide at 150—200°, the salts of the ammonium base



$$\mathrm{C_6H_3Me}\!<\!\begin{array}{c}\mathrm{N}\\ \mathrm{S}\end{array}\!\!>\!\mathrm{C\cdot C_6H_4\cdot NMe_3\cdot OH}$$

are formed; the chloride has been introduced into the market under the name *thioflavin*, and is a similar dye to auramine. The primuline base is prepared by heating thiotoluidine or dehydrothiotoluidine, or even paratoluidine, with sulphur; its constitution has not yet been established. Treatment with fuming sulphuric acid converts it into the sulphonic acid, the sodium salt of which is primuline. (For the similar dyes obtained from metaxylidine and pseudocumidine, see Abstr., 1889, 602.) Dehydrothioxylidine unites with α-naphthol-α-sulphonic acid, forming the dye named "*Erika.*" *Thiazole-yellow* is sodium amidoazodehydrothiotoluidinesulphonate; it dyes unbleached fibre greenish-yellow and cannot be deazotised on the fibre.

J. W. L.

Parachloracetotoluidide and Metaparanitrochloracetotoluide. By H. ECKENROTH and A. DONNER (*Ber.*, **23**, 3287—3289).—Parachloracetotoluidide has previously been obtained by the action of chloracetic chloride on paratoluidine, and may be prepared by heating paratoluidine (1 mol.) with chloracetic acid (2 mols.) at 80—90° for two hours; the product is treated with water and recrystallised from alcohol. If the temperature is allowed to rise somewhat, a second compound is formed, which is being further investigated; it is sparingly soluble in water, but dissolves in dilute potash, and is precipitated by hydrochloric acid; from alcohol, it crystallises in white needles melting above 230° with decomposition.

Nitrochloroacetotoluidide, $NO_2\cdot C_6H_3Me\cdot NH\cdot CO\cdot CH_2Cl$

$$[\mathrm{Me} : \mathrm{NO_2} : \mathrm{NH} = 1 : 3 : 4],$$

is prepared by the action of nitric acid at ordinary temperatures on the chloracetic derivative, and crystallises from alcohol in yellow needles which melt at 122° and yield metaparanitrotoluidine on treatment with potash. J. B. T.

Action of Potassium Hypobromite on Phenylsuccinamide. By S. Hoogewerff and W. A. van Dorp (*Rec. Trav. Chim.*, 9, 33—68).—In a previous communication (Abstr., 1889, 981), the authors have shown that chlorine, bromine, hydroxyl, and nitrosyl are extremely mobile when combined with nitrogen, compounds containing such a combination readily undergoing an intramolecular change, in which the negative element or group is displaced by a more positive radicle. In continuation of these researches, they have investigated the action of potassium hypobromite on phenylsuccinamide, and the properties of the bromamido-compound thus obtained.

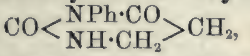
The phenylsuccinamide required for these experiments was prepared by the method given by Menschutkin (this Journal, 1872, 497). 15 grams of this substance is dissolved in a solution of 18 grams of potash and 12 grams of bromine in 300 c.c. of water, then diluted with 600 c.c. of water, acidified with acetic acid, and the precipitate thus obtained washed with water. The product could not be obtained pure, but was found to contain bromine, and from its reactions is undoubtedly a *bromamidophenylsuccinamide*, $NHBr{\cdot}C_4H_4O_2{\cdot}NHPh$. On warming its solution in alcohol or acetone, an intramolecular change takes place, *parabromophenylsuccinamide*, $NH_2{\cdot}C_4H_4O_2{\cdot}NH{\cdot}C_6H_4Br$, being formed. The latter is sparingly soluble in cold water and ether, more readily in hot water, and very easily in boiling alcohol and acetone. It crystallises in needles or plates which melt at 213—215° with decomposition. On boiling with aqueous potash, it yields first parabromophenylsuccinamic acid and ammonia, the former decomposing on further heating with potash into parabromaniline and succinic acid. *Parabromophenylsuccinamic acid* crystallises in needles, melts at 186—187°, and is readily soluble in alcohol and acetone, sparingly in ether and water. It may also be prepared by the action of alkaline potassium hypobromite on phenylsuccinamic acid. Its *barium* salt forms needles or plates, and its *copper* salt is a pale-blue precipitate.

By the action of warm dilute potash on bromamidophenylsuccinamide, the bromine is displaced by hydroxyl, and an intramolecular change takes place at the same time. To carry out the reaction, 10 grams of phenylsuccinamide are converted into the bromamide, and the latter is dissolved in a solution of 6 grams of potash in 34 c.c. of water, 50 c.c. of concentrated potash solution is then added, and the whole warmed for $2\frac{1}{2}$ hours at 55—60°. On the addition of hydrochloric acid, a precipitate is obtained, which is purified by dissolving it in potash, reprecipitating with hydrochloric acid, reducing its alkaline solution with sodium amalgam, and recrystallising from hot water. Its composition was found on analysis to be $C_{10}H_{12}N_2O_3$. On passing hydrogen chloride into its alcoholic solution and adding sulphuric acid, it very readily yields an ethyl salt, and therefore contains a carboxyl group. It loses the elements of water on boiling with acetic chloride, forming a substance which is reconverted by alkalis into the original compound, and on fusion with potash decomposes into carbonic anhydride, aniline, and β-amidopropionic acid. From these facts, it follows that the acid has the constitution

$$NHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

and it may be termed *phenyl-β-ureïdopropionic acid* or *phenyl-β-lacturamic acid.* It crystallises in needles or plates melting when quite pure at 171—172°, and is readily soluble in alcohol, acetone, warm water, and warm acetic acid, sparingly in ether, and almost insoluble in benzene and light petroleum. The *calcium* salt, $(C_{10}H_{11}N_2O_3)_2Ca$, forms concentrically grouped needles, and the *silver* salt, $C_{10}H_{11}N_2O_3Ag$, an amorphous, white precipitate, which is fairly stable towards light. The *ethyl* salt, $C_{10}H_{11}N_2O_3Et$, crystallises from water containing a little sodium carbonate, in needles, melts at 84—85°, and is readily soluble in alcohol, ether, and benzene, sparingly in light petroleum.

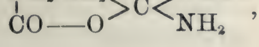
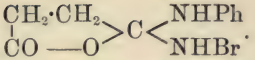
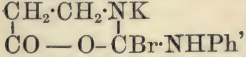
As already stated, the acid is split up on fusion with potash into carbonic anhydride, aniline, and β-amidopropionic acid. The latter is best isolated as the platinochloride of its ethyl salt, which is obtained by passing hydrogen chloride into the alcoholic solution of the acid, evaporating, and treating the alcoholic solution of the residue with platinic chloride solution. It separates in yellow needles, containing water of crystallisation which is given off at 90—100°, the salt then having the composition $(C_5H_{11}NO_2)_2,H_2PtCl_6$. It is readily soluble in water, melts at 193° with evolution of gas, and is identical with the compound prepared synthetically from β-iodopropionic acid. The *hydrochloride*, $C_5H_{11}NO_2,HCl$, forms hygroscopic crystals.

The compound obtained by the action of acetic chloride on phenylureïdopropionic acid has the composition $C_{10}H_{10}N_2O_2$, and crystallises in needles which melt at 231—234°, and do not volatilise without decomposition. It stands in the same relation to phenylureïdopropionic acid as hydantoïn to hydantoïc acid, and has, therefore, the constitution  $CO{<}{\genfrac{}{}{0pt}{}{NPh{\cdot}CO}{NH{\cdot}CH_2}}{>}CH_2$, and may be termed *phenylhydrouracil.* By the further action of acetic chloride at 100°, or by acting with an excess of the latter on the acid, *phenylacetylhydrouracil*, $C_{12}H_{12}N_2O_3$, is obtained, and crystallises in needles melting at 135—138°.

That phenylureïdopropionic acid has really the constitution above assigned to it has been further shown by its synthetical formation from phenylcarbamide and β-amidopropionic acid. On heating these two compounds together at 135°, the following reaction takes place:—

$$NHPh{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH = NHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + NH_3.$$

The compound thus obtained is identical in all respects with the acid above described, but the yield is not good.

The formation of phenyl-β-ureïdopropionic acid from phenylsuccinamide is very difficult, and perhaps impossible, to explain, if the latter has the symmetrical constitution usually assigned to it, namely, $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NHPh$. It has, however, been shown by Auger (Abstr., 1888, 952) that asymmetrical succinamide can exist, and the authors believe that phenylsuccinamide has also the asymmetrical constitution  $\genfrac{}{}{0pt}{}{CH_2{\cdot}CH_2}{CO{-\!-}O}{>}C{<}\genfrac{}{}{0pt}{}{NHPh}{NH_2}$, the bromamido-compound then becoming  $\begin{array}{l} CH_2\cdot CH_2 \\ | \\ CO - O \end{array}\!\!>C<\!\!\begin{array}{l} NHPh \\ NHBr \end{array}$. The potassium salt of the latter undergoes an intramolecular change, forming the compound  $\begin{array}{l} CH_2\cdot CH_2\cdot NK \\ |\qquad\qquad | \\ CO - O - CBr\cdot NHPh \end{array}$, which by the further action of potash yields $COOK\cdot CH_2\cdot CH_2\cdot NH\cdot C(OH)(OK)\cdot NHPh$; this then loses the elements of KOH, forming phenyl-β-ureïdopropionic acid,

$$COOK\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot NHPh.$$

When parabromophenylsuccinamide is treated with potassium hypobromite, it yields an unstable bromamide, which is readily converted into the corresponding *bromophenylureïdopropionic acid*, $C_{10}H_{11}BrN_2O_3$, by the action of potash. This acid is readily soluble in warm alcohol, sparingly in ether, benzene, and hot water, and crystallises in flat needles which decompose at 229°. On fusion with potash, it yields parabromaniline, and its alkaline solution is reduced by sodium amalgam to phenylureïdopropionic acid. Its *calcium* salt is a very voluminous precipitate, and its *silver* salt forms white flocks.

By the action of potassium hypobromite (1 mol.) on phenylureïdopropionic acid, no monobromo-compound could be obtained, but with 2 mols. of hypobromite, a small quantity of *dibromophenylureïdopropionic acid*, $C_{10}H_{10}Br_2N_2O_3$, was formed, crystallising in needles which melt at 201—202° and yielding dibromaniline (m. p. 78—81°) on fusion with potash. If 3 mols. of hypobromite are employed, *tribromophenylureïdopropionic acid*, $C_{10}H_9Br_3N_2O_3$, is obtained, and is also formed in smaller quantity with the dibromo-compound when only 2 mols. of hypobromite are used. It separates from acetic acid in crystals which melt at 219—220° with decomposition, and yields symmetrical tribromaniline on fusion with potash. H. G. C.

Carbamide Derivatives of Amidocinnamic Acid. By F. W. Rothschild (*Ber.*, **23**, 3341—3346).—*Orthouramidocinnamic acid*, $NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH$, is prepared by the action of potassium cyanate on orthamidocinnamic acid hydrochloride, and crystallises from water in small, pale-yellow needles which dissolve in ammonia and also in hydrochloric acid; the aqueous solution has an acid reaction.

Orthamidocinnamic acid thiocyanate,

$$CNSH,NH_2\cdot C_6H_4\cdot CH{:}CH\cdot COOH,$$

is obtained in a similar manner to the previous compound, and is deposited from water in tufts of prismatic crystals which melt at 152° with evolution of gas. On heating the compound at 110—120° for 18 hours, *orthothiouramidocinnamic acid*,

$$NH_2\cdot CS\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH,$$

is formed, which melts at 236—239°, and is insoluble in alcohol, but dissolves in hot glacial acetic acid or ammonia.

Orthoallylthiouramidocinnamic acid,

$$C_3H_5\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot CH{:}CH\cdot COOH,$$

crystallises from a small quantity of acetic acid on the addition of water in white needles which melt at 204—208° with decomposition.

Orthophenylthiouramidocinnamic acid,

$$NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot CH:CH\cdot COOH,$$

crystallises from glacial acetic acid, and melts at 235—237°.

By the action of carbon bisulphide on orthamidocinnamic acid at 100°, a compound is obtained which is probably *orthocarbocinnamyldithiocarbamic acid*, $CSSH\cdot NH\cdot C_6H_4\cdot CH:CH\cdot COOH$; it crystallises from water in white, microscopic prisms, melts at 185—187°, and is soluble in ammonia but insoluble in hydrochloric acid.

Metathiocyanamidocinnamic acid is prepared by the action of thiocyanic acid on metamidocinnamic acid; it crystallises from alcohol, melts at 148—149°, and is very readily soluble in water and alcohol in the cold. The corresponding *para-derivative* crystallises from water in pale, yellowish-brown needles, which remain unmelted at 272°, but decompose on suddenly heating. It yields a white silver salt. On evaporating an aqueous solution, and heating the residue for some time at 100°, *parathiouramidocinnamic acid* is obtained as a yellow substance insoluble in alcohol; it remains solid at 273°, but melts with gas evolution when heated on platinum foil. J. B. T.

Aromatic Alkyl Ketones; their Oxidation by Potassium Permanganate. By A. Claus (*J. pr. Chem.* [2], **42**, 508—516; compare Abstr., 1890, 769, 979).—*Paracymyl methyl ketone* [Me : Ac : Pr = 1 : 2 : 4] is a nearly colourless oil which boils at 249—250° (uncorr.), and does not solidify at −10°. The *oxime* was obtained. The *phenylhydrazide* forms lustrous, colourless needles which melt at 134° (uncorr.). By reduction with zinc-dust in alcoholic potash, the ketone yields *paracymylmethylcarbinol* [Me : Pr : CHMe·OH = 1 : 4 : 2], an uncrystallisable oil which boils above 300°. The constitution of this ketone is settled by the fact that it yields methylisophthalic acid [Me : $(COOH)_2$ = 1 : 2 : 4] (m. p. 332°), identical with Jacobsen's β-xylidenic acid (Abstr., 1882, 188); the *potassium* (with 2 mols. H_2O), *barium* (with 2 mols. H_2O), and *silver* (with 1 mol. H_2O) salts of this acid, and the *chloride*, and the *amide* are described; further oxidation converts this acid into trimellitic acid [1 : 2 : 4] (m. p. 210°, uncorr.).

Paracymylglyoxylic acid [Me : CO·COOH : Pr = 1 : 2 : 4], obtained by oxidising the ketone in the cold with potassium permanganate, is a thick, yellow oil; it decomposes at 220°, and dissolves in the usual solvents except water; the *calcium* (with 2 mols. H_2O), *barium* (with 1 mol. H_2O), and *silver* salts were obtained. When reduced with sodium amalgam, this acid yields *paracymylglycollic acid*

$$[Me : CH(OH)\cdot COOH : Pr = 1 : 2 : 4],$$

which forms crystals melting at 124° (uncorr.), and soluble in the usual solvents, except cold water; the *sodium, potassium, calcium* (with $2\frac{1}{2}$ mols. H_2O), *barium* (with 3 mols. H_2O), *silver, copper* (with 8 mols. H_2O), and *lead* salts are described.

By heating paracymyl methyl ketone with ammonium sulphide in a sealed tube *paracymylacetamide* [Me : Pr : CH_2CONH_2 = 1 : 2 : 4] is obtained; this crystallises in thin, lustrous scales, melts at 123° (uncorr.), sublimes, and dissolves in the usual solvents, except cold water. *Paracymylacetic acid* is obtained by saponifying the amide; it crystallises in flat, lustrous, colourless needles which melt at 70° (uncorr.), and dissolve in the usual solvents, except cold water; the *sodium* (with 2 mols. H_2O), *potassium* (with 1½ mols. H_2O), *calcium* (with 4 mols. H_2O), *barium* (with 6 mols. H_2O), and *silver* salts are described.

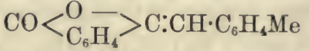
A. G. B.

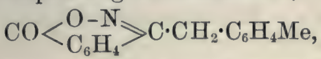
Benzoic Fluoride. By E. GUENEZ (*Compt. rend.*, **111**, 681—682).—This compound can be prepared by Moissan's reaction. Silver fluoride and benzoic chloride in equivalent proportions are heated in a sealed tube at 190° for five to six hours. The product is distilled from the silver chloride, and even if excess of silver fluoride has been used, the liquid must be heated again in a sealed tube with more silver fluoride, in order to ensure the complete decomposition of the benzoic chloride.

Benzoic fluoride is a colourless liquid with an odour resembling that of benzoic chloride, but much more irritating. It boils at 145°, burns with a smoky flame with a blue edge, is heavier than water, by which it is decomposed into benzoic and hydrofluoric acids, and is rapidly decomposed by solutions of alkalis, especially on heating. Benzoic fluoride attacks glass with great rapidity, with formation of silicon fluoride, an alkaline fluoride, and benzoic anhydride. C. H. B.

Conversion of Cinnamic into Isocinnamic Acid. By E. ERLENMEYER (*Ber.*, **23**, 3130—3131).—Since both α- and β-bromocinnamic acid yield benzaldehyde on oxidation, the bromine atom must be in the α-position in both compounds; it is probable, therefore, that the so-called β-bromocinnamic acid corresponds with isocinnamic acid and the α-bromo-acid with cinnamic acid. This view is rendered very probable by the fact that when the β-acid is treated with hydrogen under certain conditions, it yields isocinnamic acid and variable quantities of cinnamic acid; the iso-acid obtained in this way exhibits all the properties of the natural isocinnamic acid discovered by Liebermann.

F. S. K.

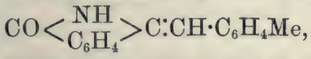
Metaxylalphthalide. By E. HEILMANN (*Ber.*, **23**, 3157—3168).—Metatoluylacetic acid is prepared by heating metatoluylacetonitrile with three parts of concentrated hydrochloric acid at 100° for 4—5 hours. On fusing metatoluylacetic acid with an equal weight of phthalic anhydride, together with a small quantity of anhydrous sodium acetate, water and carbonic anhydride are eliminated, and a substance with the formula  $CO{<}^{O\,—}_{C_6H_4}{>}C{:}CH{\cdot}C_6H_4Me$ is formed; if the group $CH{\cdot}C_6H_4Me$ is termed *xylal*, then this compound would be called *metaxylalphthalide*. It crystallises from alcohol in pale-yellow needles melting at 152—153°, and is very sparingly soluble in the ordinary media; the yield is 64 per cent. of the theory. On treatment with potash, xylalphthalide is hydrolysed, and the unsaturated acid which is first formed changes spontaneously into the compound $C_6H_4Me{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$; this is deposited from alcohol on the addition of water, in long, lustrous crystals which melt at 111—112°. The corresponding *oximidolactone*,



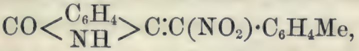
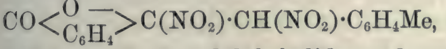
$$CO<\genfrac{}{}{0pt}{}{O-N}{C_6H_4}>C\cdot CH_2\cdot C_6H_4Me,$$

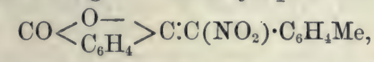
is prepared by the action of hydroxylamine on the acid, and crystallises from dilute alcohol in white, lustrous needles which melt at 133—134°, and are insoluble in alkalis.

By the action of alcoholic ammonia on xylalphthalide, *methyldeoxybenzoïncarboxylamide* is formed; it is difficult to isolate and readily loses the elements of water, *metaxylalphthalimidine*,



$$CO<\genfrac{}{}{0pt}{}{NH}{C_6H_4}>C\colon CH\cdot C_6H_4Me,$$

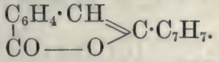
being obtained; this crystallises from alcohol in needles which melt at 165°. *Nitro-xylalphthalimidine*,  $CO<\genfrac{}{}{0pt}{}{C_6H_4}{NH}>C\colon C(NO_2)\cdot C_6H_4Me$, is prepared by the action of nitrous acid on xylalphthalimidine; it crystallises from alcohol in yellow, lustrous needles, and melts at 157—159°. The reaction is explained by assuming that an unstable dinitro-derivative is first formed, from which the mononitro-compound is produced by the elimination of nitrous acid. *Dinitro-xylalphthalide*,  $CO<\genfrac{}{}{0pt}{}{O\ -}{C_6H_4}>C(NO_2)\cdot CH(NO_2)\cdot C_6H_4Me$, is prepared by the action of nitrous acid on xylalphthalide, and crystallises from acetic acid in white, lustrous, rhombohedral plates, which soften at 125° and melt at 133° with evolution of gas. *Nitro-xylalphthalide*,

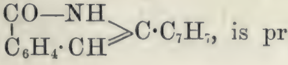


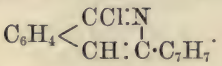
$$CO<\genfrac{}{}{0pt}{}{O-}{C_6H_4}>C\colon C(NO_2)\cdot C_6H_4Me,$$

is prepared by heating the previous compound with dilute alcohol; it crystallises in yellow, lustrous needles, and melts at 144° with decomposition.

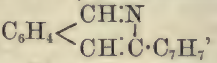
Nitro-xylalphthalide is dissolved in potash, and the solution acidified with hydrochloric acid; the product consists of a mixture of phthalic anhydride and *metatoluylnitromethane*, $C_6H_4Me\cdot CH_2\cdot NO_2$; this compound is separated by distillation in a current of steam, and is a yellow, viscid liquid which decomposes on distillation, has a peculiar, offensive smell, and yields metaxylylamine on reduction.

Nitro-xylalphthalide is decomposed on heating at 190°, phthalic anhydride and *metatoluyl isocyanate* being formed; the latter is a colourless, oily liquid, which boils at 190—200°, and yields metatoluylcarbamide on treatment with ammonia; the vapour rapidly attacks the eyes. By the action of phosphorus and hydriodic acid on nitroxylalphthalide, a compound is obtained which is isomeric with xylalphthalide, and is therefore termed *iso-xylalphthalide;* it is slowly deposited from alcohol in long, slender, white crystals, which melt at 92—93°. The constitution of the compound is probably represented by the formula  $\genfrac{}{}{0pt}{}{C_6H_4\cdot CH}{CO - O}>C\cdot C_7H_7$.

Iso-xylalphthalimidine,  $\genfrac{}{}{0pt}{}{CO-NH}{C_6H_4\cdot CH}>C\cdot C_7H_7$, is prepared by heating the previous compound with alcoholic ammonia at 100°; crystallises in small, lustrous needles, melts at 196°, and is very sparingly soluble in the ordinary media. *Metatoluylchloroisoquinoline*,



$$C_6H_4<\begin{matrix}CCl:N\\ CH:C\cdot C_7H_7\end{matrix}$$

is obtained by the action of phosphorus oxychloride on the previous compound; it crystallises in white, lustrous needles, and melts at 43—44°. On heating with hydriodic acid at 170°, and treating the product with potash, *metatolylisoquinoline*,  $C_6H_4<\begin{matrix}CH:N\\ CH:C\cdot C_7H_7\end{matrix}$, is formed as a colourless, viscid liquid, which crystallises after some time, and melts at 51—52; it is deposited from methyl alcohol in long, lustrous needles. The *picrate*, *hydrochloride*, *sulphate*, and *platinochloride* are all crystalline. J. B. T.

Isogallic Acid Phenylhydrazide. By C. Böttinger (*Annalen*, **259**, 373—377).—The phenylhydrazine derivatives of tannin and gallic acid (Abstr., 1890, 163) are very similar in properties, and have the same reducing power as regards alkaline copper solutions; when the tannin derivative is heated with hydrochloric acid at 120°, it is decomposed into gallic acid, phenylhydrazine, and a very small quantity of a reddish-yellow, crystalline, neutral substance; the author names it, therefore, isogallic acid phenylhydrazide.

Isogallic acid phenylhydrazide is converted into an unstable acetyl derivative on boiling with acetic anhydride; it is completely decomposed by boiling alkalis, a property which it has in common with gallic acid phenylhydrazide. F. S. K.

Condensation Products of Amido-acids with Benzenesulphonic Chloride. By S. G. Hedin (*Ber.*, **23**, 3196—3199; see also Hinsberg, this vol., p. 49).—For the preparation of the above condensation products, the amido-acid is dissolved in aqueous potash, and an equivalent quantity of benzenesulphonic chloride added in small portions alternately with caustic potash, warming and shaking well during the process. After filtering, if necessary, the liquid is acidified, and the product, being, as a rule, sparingly soluble in cold water, may then be readily purified.

Alanine yields the compound $SO_2Ph\cdot NH\cdot C_2H_4\cdot COOH$, crystallising from hot water in slender needles; this melts at 126°, but forms an oil under water at 100°, and is readily soluble in hot water, alcohol, ether, and ethyl acetate.

The *leucine* compound, $SO_2Ph\cdot NH\cdot C_5H_{10}\cdot COOH$, crystallises in beautiful, long needles which melt at 86°, and are less soluble in water than the foregoing compound, but readily soluble in alcohol, ether, acetic acid, and chloroform.

The *aspartic acid* derivative, $SO_2Ph\cdot NH\cdot C_2H_3(COOH)$, crystallises in splendid, rhomboïdal crystals melting at 170°.

The *alutamine* compound, $SO_2Ph\cdot NH\cdot C_3H_5(COOH)_2$, does not separate on the addition of an acid, but must be extracted with ether, and on the evaporation of this it remains as a syrup which gradually solidifies over sulphuric acid, but is not thus obtained quite pure. It is distinguished from the other condensation products by its ready solubility in water.

Tyrosine yields two compounds, one of which is sparingly, and the other readily, soluble in water. The former has the composition $SO_2Ph{\cdot}NH{\cdot}C_2H_3(C_6H_4{\cdot}OH){\cdot}COOH$, but the latter has not been obtained pure.

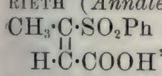
Tolueneparasulphonic chloride also readily forms condensation products with amido-acids. Moreover, fibrin, after treatment with pancreatic juice, combines with benzenesulphonic chloride, forming an oil, but it is uncertain whether this is a mixture or not.

An attempt was made to prepare *benzenesulphoneglycocine*, $SO_2Ph{\cdot}NH{\cdot}CH_2{\cdot}COOH$, by feeding dogs with sodium benzenesulphonate, a process corresponding to the preparation of hippuric acid from sodium benzoate. The results obtained, however, were negative, as were similar experiments in the human organism. H. G. C.

Benzenesulphinic Acid and Ethylsulphinic Acid. By W. Autenrieth (*Annalen*, **259**, 362—364).—Pure, dry benzenesulphinic acid does not readily undergo oxidation on exposure to the air; its sodium salt is very stable, and is not decomposed to any appreciable extent when its aqueous solution is heated at 180° for 12 hours.

Ethylsulphinic acid is best prepared by oxidising ethyl mercaptan with potassium permanganate, converting the sulphonic acid thus produced into the chloride, and reducing the latter with zinc-dust in alcoholic solution. The pure acid is unstable, but the dry sodium salt is only slowly oxidised on exposure to the air. F. S. K.

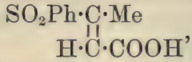
Sulphone Derivatives of the Crotonic Acids. By W. Autenrieth (*Annalen*, **259**, 332—357).—*β-Phenylsulphoneisocrotonic acid*,

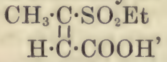


$$\begin{array}{l}CH_3{\cdot}C{\cdot}SO_2Ph\\ \quad\ \|\\ H{\cdot}C{\cdot}COOH\end{array}$$

, can be prepared by heating a moderately concentrated aqueous solution of sodium β-chlorisocrotonate with sodium benzenesulphinate at 140—150° for six to eight hours, precipitating the acid with sulphuric acid, and then extracting with ether. It can also be obtained by treating ethyl β-diphenylsulphonebutyrate with cold, concentrated potash (compare next abstract); the yield is almost quantitative in both cases. It crystallises from water in needles, melts at 126—127°, and decomposes at a higher temperature; it is moderately easily soluble (1 in 20) in boiling, but only sparingly (1 in 390 at 15°) in cold, water. It is decomposed by tin and warm concentrated hydrochloric acid with liberation of mercaptan, and boiling alkalis decompose it completely with elimination of benzenesulphinic acid, but it is not acted on by bromine in boiling chloroform solution. The *potassium* salt, $C_{10}H_9SO_4K + 3H_2O$, crystallises from water in large, transparent, efflorescent plates, and is readily soluble in water and alcohol. The *barium* salt, $(C_{10}H_9SO_4)_2Ba + 2\frac{1}{2}H_2O$, *magnesium* salt (with 6 mols. H_2O), and *zinc* salt (with 6 mols. H_2O) crystallise well, and are moderately easily soluble in water.

The *silver* salt, $C_{10}H_9SO_4Ag$, crystallises from water in well-defined plates, and decomposes suddenly at 240—245°. The *ethyl* salt, $C_{10}H_9SO_4Et$, is a colourless oil.

β-Phenylsulphonecrotonic acid,  $\begin{array}{c}\mathrm{SO_2Ph{\cdot}C{\cdot}Me}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, is prepared by heating an aqueous solution of the sodium salt of β-chlorocrotonic acid with sodium benzenesulphinate at 160—180° for eight hours; the yield is quantitative. It crystallises from water in lustrous plates, melts at 158° with previous softening, and is moderately easily soluble in ether, alcohol, and benzene, but only very sparingly in light petroleum; it is soluble in 262 parts of water at 15° and in 3·8 to 4 parts of boiling water. When heated at 200—210° for 20 hours, it is completely converted into the isomeride (m. p. 127°) described above, but attempts to bring about this intramolecular change by means of sulphuric acid, iodine, alcohol, and water were unsuccessful. The *potassium* salt, $C_{10}H_9SO_4K + 1\frac{1}{2}H_2O$, is deliquescent, and does not crystallise well. The *barium* salt, $(C_{10}H_9SO_4)_2Ba + H_2O$, is very readily soluble in water. The *magnesium* salt (with 7 mols. H_2O) and the *zinc* salt (with 6 mols. H_2O) separate from water in large, transparent crystals. The *copper* salt forms small crystals containing 1 mol. H_2O. The *silver* salt, $C_{10}H_9SO_4Ag$, crystallises from water in very small needles, and decomposes suddenly at 198—200°.

β-Ethylsulphoneisocrotonic acid,  $\begin{array}{c}\mathrm{CH_3{\cdot}C{\cdot}SO_2Et}\\ \|\\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, can be prepared by treating ethyl β-diethylsulphonebutyrate (compare Baumann, Abstr., 1887, 123) with potash in the cold, or by heating sodium β-chlorisocrotonate at 140—150° with sodium ethylsulphinate in aqueous solution. It separates from cold water in well-defined crystals, melts at 98°, and is readily soluble in alcohol, ether, chloroform, and water, but only moderately easily in benzene. It is slowly decomposed by alkalis into tetrolic acid and ethylsulphinic acid, and when treated with tin and hydrochloric acid it yields mercaptan, but it is not acted on by bromine in boiling chloroform solution. The *silver* salt, $C_6H_9SO_4Ag$, forms large, well-defined crystals, and decomposes on exposure to light; the other metallic salts do not crystallise well. The *ethyl* salt, $C_8H_{14}SO_4$, is a colourless oil which cannot be distilled. The stereochemical isomeride of β-ethylsulphoneisocrotonic acid could not be obtained. F. S. K.

Sulphur Derivatives of Ethyl Acetoacetate, Ethyl Methylacetoacetate, and Ethyl Ethylacetoacetate. By W. AUTENRIETH (*Annalen,* **259**, 365—373).—*Ethyl β-diphenylsulphonebutyrate,* $CMe(SO_2Ph)_2{\cdot}CH_2{\cdot}COOEt$, can be obtained by adding sulphuric acid and potassium permanganate to a benzene solution of ethyl β-dithiophenylbutyrate (compare Baumann and Escales, Abstr., 1886, 878) until a permanent coloration is produced. It separates from alcohol in well-defined, lustrous crystals, melts at 97°, and is readily soluble in hot alcohol, ether, and benzene, but only sparingly in cold alcohol, and insoluble in water; when treated with potash, it is converted into β-phenylsulphoneisocrotonic acid (compare preceding abstract).

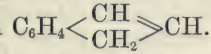
Ethyl α-ethyl-β-diethylsulphonebutyrate, $CMe(SO_2Et)_2{\cdot}CHEt{\cdot}COOEt$, is formed when ethyl α-ethyl-β-dithioethylbutyrate, the condensation product of ethyl mercaptan and ethyl ethylacetoacetate, is oxidised in a similar manner. It crystallises from boiling water in lustrous plates, melts at 87—88°, and is readily soluble in ether, benzene, and alcohol; it is not acted on by concentrated potash or ammonia in the cold, but on boiling with potash, it is gradually decomposed, yielding small quantities of an acid melting at 102—103°, the nature of which could not be determined.

Ethyl α-methyl-β-diethylsulphonebutyrate, prepared in like manner, crystallises from water in plates, melts at 79°, and is only sparingly soluble in cold, but readily in hot, water; it is not acted on by cold alkalis, but when boiled therewith, it is completely decomposed.

Ethyl α-ethyl-β-dithiophenylbutyrate, $CMe(SPh)_2{\cdot}CHEt{\cdot}COOEt$, is obtained when hydrogen chloride is passed into a mixture of ethyl ethylacetoacetate and phenyl mercaptan. It separates from alcohol in large, transparent crystals, melts at 70—71°, and is readily soluble in benzene, alcohol, and ether, but insoluble in water.

Ethyl α-ethyl-β-diphenylsulphonebutyrate, $C_{20}H_{24}S_2O_6$, prepared by oxidising the preceding compound in the manner described above, separates from alcohol in crystals, melts at 111°, and is insoluble in water, but readily soluble in alcohol, benzene, and ether; when boiled with potash, it yields only a trace of an acid. F. S. K.

Indene and Cinnamene in Coal-tar. By G. KRAEMER and A. SPILKER (*Ber.*, **23**, 3276—3283; compare Abstr., 1890, 496).—The higher fractions of the light oils obtained from coal-tar contain a hydrocarbon of the composition C_9H_8, to which the authors give the name *indene*, as it has the constitution



$C_6H_4<\begin{matrix}CH\\CH_2\end{matrix}>CH$.

This compound is isolated in the following manner from the fractions boiling at 176—182°, the yield of the pure substance being about 20 per cent. of the crude oil employed:—A quantity of picric acid, sufficient to combine with the unsaturated compounds (determined by titrating a portion of the oil with bromine), is dissolved in the hot liquid, the crystalline precipitate, which contains as impurities all the naphthalene and a little cumarone, is treated with steam, and the indene in the distillate purified by precipitation with picric acid in toluene solution. The picrate is obtained in this way in golden needles melting at 98°; it decomposes slowly on exposure to the air, but quickly when heated with water, and it explodes when heated in the dry state.

Indene is a colourless oil of sp. gr. 1·04 at 15°, which turns yellowish on keeping, the colour disappearing again on exposure to light; it boils at 179·5—180·5° (corr.), is converted into a resinous compound (parindene) by concentrated sulphuric acid in benzene or ethereal solution, and into a very insoluble, infusible substance, which contains a large quantity of sulphur, by energetic treatment with concentrated sulphuric acid. On oxidation with boiling 30 per cent. nitric acid, it yields phthalic acid. The *dibromide*, $C_9H_8Br_2$, prepared by treating the hydrocarbon with the theoretical quantity of bromine in ethereal solution, forms transparent, prismatic crystals, melts at 43—45°, and is readily soluble in all ordinary solvents except water and light petroleum; it readily undergoes spontaneous decomposition with evolution of hydrogen bromide and formation of a resinous substance.

Indene hydroxybromide, C_9H_9BrO, is formed when the dibromide is warmed with water or boiled with 10 per cent. alcohol; it crystallises in colourless needles, melts at 130—131°, and is soluble in water and alcohol.

Hydrindene, C_9H_{10}, is obtained when indene is reduced with sodium and alcohol; it is a colourless oil of sp. gr. 0·957 at 15°, and boils at 176—176·5° (corr.). It forms a sulphonic acid, the salts and amide of which are very like the corresponding derivatives of benzenesulphonic acid.

Cinnamene can be isolated from coal-tar in the form of the crystalline dibromide, $C_8H_8Br_2$, by treating well-cooled, crude xylene with bromine and evaporating the solution.

The red coloration which is produced on dissolving impure naphthalene in sulphuric acid is due to the presence of indene, and the red coloration observed in the case of phenol is probably due to a similar cause. F. S. K.

Synthesis of Indigo with Phenylglycocine. By K. Heumann (*J. pr. Chem.*, [2], **42**, 520).—The author claims priority as to the method for the synthesis of indigo published by Lederer (this vol., p. 75), he having already patented the method. Lederer is mistaken in supposing that indigo is left when the melt is dissolved in water or dilute sulphuric acid; any that may be formed is only produced by oxidation by the air; some substance like indigo-white is the actual product of the fusion, and oxidation is necessary to convert this into indigo. The author is further investigating the subject.

A. G. B.

Synthesis of Indigo from Anilidoacetic Acid. By A. Biedermann and R. Lepetit (*Ber.*, **23**, 3289—3291).—Aniline and chloracetic acid are mixed together in molecular proportions and fused with 3—4 parts of soda, together with sufficient water to form a paste; as soon as the mass becomes orange-coloured, it is quickly cooled, dissolved in water, and the solution oxidised by means of a current of air; indigo is at once deposited, the yield being 9·5 per cent. It is probable that in the first instance anilidoacetic acid is formed; two molecules then combine together with elimination of water and hydrogen. Indigo may also be obtained by the fusion of anilidoacetic acid and sodium, the product being then oxidised with air as before. Indigo is directly prepared by the fusion of a mixture of oxanilic acid and anilidoacetic acid in molecular proportion with excess of soda; the yield is a little less than with anilidoacetic acid alone. J. B. T.

Condensation of Cinnamene with Methylbenzene Derivatives. By G. Kraemer and A. Spilker (*Ber.*, **23**, 3169—3174).—Crude xylene containing cinnamene is treated with concentrated sulphuric acid, when two layers of liquid are formed, the heavier of which contains sulphonic acids. The lighter oily portion is separated, washed with soda, and distilled in a current of steam; the residue after fractionation in a vacuum, yields *phenyltoluylpentane*, $CH_2Ph\cdot CH_2\cdot CH_2\cdot C_6H_4Me$; this is a colourless, viscid liquid which boils at 293—294°, and has a sp. gr. of 0·987 at 15°. It is probable that in the first instance cinnamene and sulphuric acid combine to form an additive compound, which then condenses with xylene according to the equation $CH_2Ph\cdot CH_2\cdot SO_4H + 2C_6H_4Me_2 = CH_2Ph\cdot CH_2\cdot CH_2\cdot C_6H_4Me + C_6H_3Me_2\cdot SO_3H + H_2O$. It is found that other methylbenzene derivatives condense with cinnamene in a similar manner, but benzene itself does not react in this way. On passing the vaporised substance through heated tubes, hydrogen and methane are eliminated, and methylanthracene (m. p. 200°) is formed; the yield is 62·5 per cent. of the substance employed.

Corresponding anthracene derivatives are obtained from the condensation products of cinnamene and toluene, metaxylene, and pseudocumene respectively.

The authors point out the bearing of their work on the theories regarding the formation of the higher boiling constituents of coal tar, and conclude with some polemical remarks on the Duismore process for the manufacture of coal gas. J. B. T.

Cinnamene Derivatives of Aromatic Hydrocarbons and their Conversion into Anthracene and Methylanthracenes. By G. Kraemer, A. Spilker, and P. Eberhardt (*Ber.*, **23**, 3269—3276; compare preceding abstract).—The compounds formed by the condensation of cinnamene with xylene are most probably $\alpha\beta$-, and not $\alpha\gamma$-derivatives of propane as was previously supposed; this view would explain their ready transformation into anthracene derivatives.

Metaxylenecinnamene (*$\alpha\beta$-phenylmetatoluylpropane*),

$$CHMePh\cdot CH_2\cdot C_6H_4Me,$$

prepared by gradually adding concentrated sulphuric acid to a mixture of metaxylene and cinnamene, is a colourless, feebly fluorescent oil of sp. gr. 0·987 at 15°; it boils at 240° under a pressure of 110 mm., and at 311—312° (corr.), and is miscible with alcohol, ether, benzene, and light petroleum, but insoluble in water. When passed through a red-hot tube, it is almost completely converted into methylanthracene (m. p. 207°).

Paraxylenecinnamene (*$\alpha\beta$-phenylmetatoluylpropane*), $C_{16}H_{18}$, obtained from paraxylene in like manner, boils at 302—303° (corr.), and resembles the preceding compound very closely.

Ortho-xylenecinnamene($\alpha\beta$-phenylorthotoluylpropane), $C_{16}H_{18}$, boils at 316—317° (corr).

Pseudocumenecinnamene (*$\alpha\beta$-phenylxylylpropane*),

$$CHMePh\cdot CH_2\cdot C_6H_3Me_2,$$

is obtained by the condensation of cinnamene with trimethylbenzene; it boils at 324° (corr.) and is readily converted into dimethylanthracene (m. p. 235°).

Toluenecinnamene ($\alpha\beta$-diphenylpropane), $CHMePh\cdot CH_2Ph$, prepared from toluene in like manner, is a colourless liquid boiling at 291—293° (corr.); when heated strongly, it yields only small quantities of anthracene.

Condensation products of benzene with cinnamene could not be obtained. F. S. K.

Condensation Products of Paranitrobenzyl Cyanide. By P. Remse (*Ber.*, **23**, 3133—3136).—A compound of the constitution $CHPh\colon C(CN)\cdot C_6H_4\cdot NO_2$ is formed when sodium ethoxide is gradually added to a mixture of paranitrobenzyl cyanide (1 mol.) and benzaldehyde (1 mol.) until a blue coloration is produced. It crystallises from alcohol in yellow needles, melts at 175—176°, and is soluble in glacial acetic acid, benzene, and chloroform, but only sparingly in alcohol and ether, and insoluble in water.

The condensation product obtained in like manner from orthonitrobenzaldehyde and paranitrobenzyl cyanide has the composition $C_{15}H_9N_3O_4$; it crystallises from glacial acetic acid in large, yellowish needles, melts at 184—185°, and is soluble in chloroform, benzene, alcohol, and ether, but insoluble in water.

Metanitrobenzaldehyde and paranitrobenzyl cyanide also condense to form a compound of the composition $C_{15}H_9N_3O_4$, which crystallises from alcohol in yellow needles, melts at 195°, and is soluble in most ordinary solvents except water.

A compound of the constitution $OMe\cdot C_6H_4\cdot CH\colon C(CN)\cdot C_6H_4\cdot NO_2$ can be obtained by treating anisaldehyde with paranitrobenzyl cyanide as described above; it crystallises from alcohol in yellow needles, melts at 165—166°, and is soluble in ether, benzene, and glacial acetic acid.

The condensation product of cinnamaldehyde and paranitrobenzyl cyanide has the constitution $CHPh\colon CH\cdot CH\colon C(CN)\cdot C_6H_4\cdot NO_2$; it crystallises from glacial acetic acid in yellow needles, melts at 205—206°, and is soluble in benzene and chloroform, but more sparingly in alcohol and ether, and insoluble in water. F. S. K.

Condensation of Unsaturated Hydrocarbons with Phenols. By W. Koenigs (*Ber.*, **23**, 3144—3146).—When a mixture of isoamylene and phenol is treated with a mixture of concentrated sulphuric acid (1 vol.) and glacial acetic acid (9 vols.) at the ordinary temperature for 1 to 2 days, a considerable quantity of parisoamylphenol is formed,

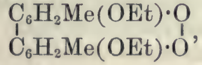
Hydroxydiphenylethane, $CHMePh\cdot C_6H_4\cdot OH$, is obtained when cinnamene is treated with phenol under the same conditions as those described above; the yield is about 40 per cent. The reaction product is submitted to distillation with steam and, as soon as the whole of the phenol has passed over, the receiver is changed, the residue heated to 160—170°, and the hydroxydiphenylmethane distilled with superheated steam; the oily product is then converted into the benzoyl derivative (m. p. 83°) by Baumann's method, and the latter, after recrystallisation from alcohol, hydrolysed with alcoholic potash. The phenol obtained in this way solidifies on cooling, and forms a sodium derivative which crystallises in colourless needles.

Resorcinol seems to yield condensation products with amylene and with cinnamene just as readily as phenol. F. S. K.

Diphenyl Derivatives from Alkylquinols. By E. Noelting and P. Werner (*Ber.*, **23**, 3246—3252).—*Diethyltoluquinol*, $C_6H_3Me(OEt)_2$, can be obtained, together with the monethyl derivative, by heating toluquinol with ethyl bromide and sodium ethoxide in alcoholic solution for 5 to 6 hours at 130—140°; the two compounds are separated by treating the product with soda, in which the diethyl derivative is insoluble. It is a colourless liquid of sp. gr. 1·0134 at 15°, boils at 247—249° (corr.), and solidifies at a low temperature, melting again at 8—9°; it is insoluble in water, but miscible with alcohol, ether, benzene, and chloroform in all proportions.

Ethyltoluquinol, $C_6H_3Me(OH)\cdot OEt$, is obtained when the alkaline filtrate from the preceding compound is acidified and then extracted with cold benzene; it crystallises from dilute alcohol in plates, melts at 116—117°, and boils at 253—287°.

Diethoxydimethyldiphenylquinone (*diethoxyditolylquinone*),



$$\begin{array}{l}C_6H_2Me(OEt)\cdot O\\ \;|\qquad\qquad\qquad\;\, |\\ C_6H_2Me(OEt)\cdot O\end{array},$$

is formed when the diethyl derivative described above is dissolved in a mixture of dilute acetic acid and sulphuric acid and a concentrated solution of sodium dichromate is gradually added. It crystallises from alcohol in greenish-black needles which melt at 139°, and, when crushed, give a reddish-brown powder; it is precipitated from its solution in boiling glacial acetic acid on the addition of water in reddish-brown flocks. It resembles very closely the cedriret-like oxidation product of the dimethyltoluquinol (compare Nietzki, Abstr., 1883, 465), than which it is, however, much more readily soluble in alcohol and glacial acetic acid.

Diethyltetrhydroxyditolyl, $OH\cdot C_6H_2Me(OEt)\cdot C_6H_2Me(OEt)\cdot OH$, prepared by reducing the preceding compound with sulphurous anhydride in boiling alcoholic solution, crystallises from dilute alcohol in colourless needles, melts at 132—133°, sublimes with partial decomposition, and readily oxidises on exposure to the air; it is only sparingly soluble in water, but moderately easily in the ordinary organic solvents.

Dimethoxyditolylquinone (compare Nietzki, *loc. cit.*) and diethoxyditolylquinone are reconverted into the corresponding quinols by phenylhydrazine, phenylhydrazinesulphonic acid, and sodium hydrogen sulphite; attempts to convert the quinols into derivatives of diphenylene oxide were unsuccessful.

Diacetyldimethoxyditolylquinol,

$$OAc\cdot C_6H_2Me(OMe)\cdot C_6H_2Me(OMe)\cdot OAc,$$

is formed when dimethoxyditolylquinol is boiled with acetic anhydride and sodium acetate; it crystallises in colourless needles, melts at 123°, and is readily soluble in glacial acetic acid, boiling alcohol, and benzene, but insoluble in water and alkalis.

Bromodimethylquinol, $C_6H_3Br(OMe)_2$, can be obtained, together with the dibromo-derivative and a liquid boiling at 246—260°, which is probably bromomethylquinol, by treating dimethylquinol with bromine (1 mol.) in cold glacial acetic acid solution; it is a colourless oil of sp. gr. 1·445 at 15°, boils at 262—263° (corr.), and is insoluble in water, but readily soluble in the ordinary organic solvents. When treated with potassium dichromate and sulphuric acid under suitable conditions, it yields a very small quantity of a cedriret-like compound, which, on reduction, is converted into a colourless, crystalline leuco-compound. The *nitro*-compound $NO_2 \cdot C_6H_2Br(OMe)_2$, prepared by nitrating with acid of sp. gr. 1·4 in well-cooled acetic acid solution, crystallises from glacial acetic acid in orange-yellow needles, and melts at 152—153°. Warm nitric acid converts dibromodimethylquinol (Habermann, *Ber.*, **11**, 1137) into a nitro-compound, which crystallises in orange prisms and melts at 188°.

Dibromodimethylquinol, nitrobromodimethylquinol, nitrodibromodimethylquinol, and nitrodimethylquinol cannot be converted into cedriret-like compounds.

Dimethylparaxyloquinol, $C_6H_2Me_2(OMe)_2$ [$Me_2 : (OMe)_2 = 1 : 4 : 2 : 5$], prepared by heating paraxyloquinol with sodium methoxide and methyl iodide in methyl alcoholic solution for 8—10 hours, crystallises from dilute alcohol in colourless plates, melts at 108°, and is soluble in ether, but insoluble in water. The corresponding diethyl derivative melts at 111—112°, and not at 105—106°, as stated by Städel and Hölz.

Diethylmetaxyloquinol is a colourless oil boiling at 240—249°. The corresponding *ortho*-compound, $C_6H_2Me_2(OEt)_2$ [$Me_2 : (OEt)_2 = 1 : 2 : 3 : 4$], forms colourless plates, melts at 68—69°, and is readily soluble in alcohol, benzene, ether, &c., but insoluble in water. Cedriret-like oxidation products cannot be obtained from the xyloquinol derivatives described above. F. S. K.

Orthomethylbenzidine. By R. Hirsch (*Ber.*, **23**, 3222—3226).—Orthomethylbenzidine can be prepared in the following manner (compare D. R.-P. 54112):—A solution of nitrobenzene (1 part) and orthonitrotoluene (4 parts) in alcohol (5 parts) is boiled with sodium hydroxide (about 0·5 part) and zinc-dust added until the solution becomes grey or bright yellow; the alcohol is then evaporated, the residue carefully treated with a quantity of hydrochloric acid just sufficient to dissolve the zinc hydroxide, but not the organic bases, and the solution filtered. The residue, which consists principally of hydrazobenzene and its homologues, is then dissolved in warm dilute hydrochloric acid to convert these compounds into the corresponding benzidines, the excess of acid expelled from the filtered solution, the bases precipitated with sodium sulphate, and the sulphates decomposed with sodium carbonate. The mixture of the three bases (benzidine, orthotoluidine, and orthomethylbenzidine) obtained in this way is repeatedly extracted with boiling water, and the combined extracts carefully treated with dilute sulphuric acid to precipitate the sulphates of benzidine and orthomethylbenzidine; these salts are decomposed, and the mixture of bases again extracted (5 times) with boiling water (20 parts), when pure orthomethylbenzidine is deposited from the first two extracts, on cooling, in lustrous plates melting at 115°. It melts at about 90° under water, forms a diacetyl derivative melting at 310°, and a benzylidene derivative, which crystallises from alcohol in yellow plates, and melts at 217°.

F. S. K.

Diphenyl Bases. By E. NOELTING and P. WERNER (*Ber.*, **23**, 3252—3266).—*Ditolyline hydrochloride*, $C_{14}H_{16}N_2,2HCl$, is obtained, together with tolidine hydrochloride and other compounds, when orthohydrazotoluene is treated with warm concentrated hydrochloric acid (4 parts). The solution is heated to boiling, then allowed to cool, the tolidine hydrochloride and azotoluene separated by filtration, and the filtrate concentrated by evaporation; after filtering again, the solution is rendered alkaline, extracted with ether, the ether evaporated, and the residue heated at 250° until free from orthotoluidine; it is then dissolved in hydrochloric acid, the ditolyline reprecipitated from the filtered solution, extracted with ether, and converted into the hydrochloride by passing hydrogen chloride into the dried ethereal solution. This salt crystallises in colourless needles, and is very readily soluble in water, but only sparingly in hydrochloric acid; in its aqueous solutions, bromine-water produces a slight, dirty-green coloration which changes to violet. The free *base* is a colourless, flocculent compound which rapidly oxidises on exposure to the air. The *sulphate* is very readily soluble. The colouring matters obtained from ditolyline do not dye cotton fibre.

Parabromazobenzene (m. p. 82°), identical with the compound obtained by Janovsky and Erb (Abstr., 1887, 478) by brominating azobenzene, can be prepared from amidoazobenzene by Sandmeyer's method; when treated with stannous chloride in alcoholic solution, it is converted into bromodiphenyline (bromobenzidine).

Pariodazobenzene, $C_{12}H_9N_2I$, prepared in like manner, crystallises from alcohol in yellowish-brown needles, melts at 105°, and is soluble in ether and benzene, but insoluble in water. The corresponding *hydrazo*-compound crystallises in colourless needles melting at 105—106°.

Iododiphenyline hydrochloride, prepared by treating the azo-compound with stannous chloride in alcoholic solution, crystallises in colourless needles, and is readily soluble in water, but only sparingly in concentrated hydrochloric acid. Bromo- and iodo-diphenyline yield coloured azo-compounds which impart to unmordanted cotton only a very slight coloration.

When metadiiodazobenzene is treated with hot concentrated hydrochloric acid, it yields iodazobenzene and large quantities of benzidine. Azobenzeneparasulphonic acid is converted into hydrazobenzeneparasulphonic acid by hydrogen sulphide in ammoniacal solution, and not into benzidinesulphonic acid as stated by Griess (*Annalen*, **154**, 213); on treating the ammoniacal solution with hydrochloric acid, benzidine sulphate is precipitated.

Ethoxyazobenzene, $NPh{:}N{\cdot}C_6H_4{\cdot}OEt$, is converted into a base of the constitution $NH_2{\cdot}C_6H_4{\cdot}C_6H_3(OEt){\cdot}NH_2$, when it is treated with the theoretical quantity of stannous chloride and hydrochloric acid in alcoholic solution; the colouring matters obtained from this base do not dye unmordanted cotton.

Orthotolylazophenol, $C_6H_4\overset{2}{Me}\cdot\overset{1}{N}{:}\overset{1}{N}\cdot C_6H_4\cdot\overset{4}{OH}$, prepared by treating diazorthotolyl chloride (1 mol.) with an alkaline solution of phenol (1 mol.) and precipitating the product with an acid, crystallises from a mixture of benzene and light petroleum in dark-red or orange-yellow plates, melts at 102—103°, and is very readily soluble in alcohol, ether, benzene, and alcohol, but only sparingly in water and light petroleum.

Orthotolyldisazophenol, $(C_6H_4Me\cdot N_2)_2C_6H_3\cdot OH$, is obtained when a larger quantity (2 mols.) of the diazochloride is employed in the above reaction; it crystallises from alcoholic chloroform in slender, brown needles, melts at 146°, and is readily soluble in chloroform, but insoluble in water.

Orthotolylazophenetoïl, $C_6H_4Me\cdot N_2\cdot C_6H_4\cdot OEt$, prepared by treating the phenol with sodium ethoxide and ethyl bromide, crystallises from alcohol in orange plates, melts at 53°, and is only sparingly soluble in water, but readily in alcohol, ether, benzene, and chloroform; stannous chloride, in alcoholic solution, converts it into a diphenyl base from which fast dyes cannot be obtained.

Paratolylazophenetoïl, $C_{15}H_{16}N_2O$, crystallises from alcohol in large, golden plates, melts at 121—122°, and is insoluble in water and alcohol, but moderately easily soluble in cold alcohol, and readily in boiling alcohol, chloroform, &c.

Paratolylhydrazophenetoïl, $C_{15}H_{18}N_2O$, prepared by reducing the preceding compound with hydrogen sulphide in ammoniacal alcoholic solution, crystallises in colourless needles, and readily oxidises on exposure to the air; it is insoluble in water, but readily soluble in boiling alcohol. Acids do not convert it into a diphenyl base, but decompose it into toluidine and amidophenetoïl.

Phenylazorthocresetoïl, $NPh{:}N\cdot C_6H_3Me\cdot OEt$, prepared from phenylazorthocresol, crystallises from alcohol in slender, orange needles or prisms, melts at 59°, and is soluble in benzene and ether, but insoluble in water. The corresponding *hydrazo*-compound, $C_{15}H_{18}N_2O$, crystallises in colourless plates, melts at 76°, and is readily soluble in hot alcohol, but insoluble in water; it readily oxidises on exposure to the air, and it is decomposed by hydrochloric acid yielding a diphenyl base from which fast azo-dyes cannot be obtained.

Orthotolylazorthocresol, $C_6H_4\overset{2}{Me}\cdot\overset{1}{N}{:}\overset{1}{N}\cdot C_6H_3\overset{3}{Me}\cdot\overset{4}{OH}$, crystallises from alcohol in red prisms, melts at 132°, and is soluble in benzene and ether, but insoluble in water. The *hydrazo*-compound, $C_{16}H_{20}N_2O$, is a colourless, crystalline substance which melts at 78°, and readily oxidises on exposure to the air; the diphenyl base, produced from the hydrazo-compound by intramolecular change under the influence of hydrochloric acid, does not yield any colouring matters which dye unmordanted cotton fibre.

Orthotolyldisazorthocresol, $(C_6H_4Me\cdot N_2)_2C_6H_2Me\cdot OH$, crystallises in slender, brown needles, melts at 148·5°, and is insoluble in water, but soluble in alcohol, benzene, chloroform, and alcoholic soda. The *ethyl* derivative, $C_{23}H_{24}N_2O_2$, prepared by treating the phenol with sodium ethoxide and ethyl bromide, crystallises in golden needles, melts at 102°, and is soluble in chloroform, benzene, and ether, but insoluble in water and alkalis.

Paratolylazorthocresol, $C_6H_4\overset{4}{Me}\cdot\overset{1}{N}{:}\overset{1}{N}\cdot C_6H_3\overset{3}{Me}\cdot\overset{4}{O}H$, forms orange crystals, melts at 163°, and is insoluble in water, but readily soluble in alcohol, ether, chloroform, and alkalis. The *ethyl* derivative, $C_{16}H_{18}N_2O$, crystallises in orange needles, melts at 73—74°, and is readily soluble in alcohol, ether, and benzene, but insoluble in water. The *hydrazo*-compound, $C_{16}H_{20}N_2O$, prepared by reducing the ethyl derivative, crystallises in colourless needles, melts at 87°, and is readily soluble in alcohol, but insoluble in water; it readily oxidises on exposure to the air, and when treated with hydrochloric acid it does not yield a diphenyl base, but is decomposed into an azo-compound and an amido-compound.

Paratolyldisazorthocresol, $C_{21}H_{20}N_4O$, forms small, prismatic crystals, melts at 164·5°, and is insoluble in water, and only sparingly soluble in alcohol. The *ethyl* derivative, $C_{23}H_{24}N_4O$, crystallises in yellow, microscopic needles, melts at 107—108°, and is soluble in hot ether, benzene, and chloroform, but insoluble in water and alkalis.

Phenylazoparacresetoïl, $NPh{:}N\cdot C_6H_3Me\cdot OEt$, prepared by heating the corresponding phenol with ethyl iodide and sodium ethoxide in alcoholic solution, crystallises from alcohol in red plates, melts at 48°, and is soluble in ether and benzene, but insoluble in water and alkalis. The *hydrazo*-compound, $C_{15}H_{18}N_2O$, crystallises in colourless needles, melts at 105°, and is soluble in alcohol, benzene, &c., but insoluble in water.

Methylethoxybenzidine, $NH_2\cdot C_6H_4\cdot C_6H_2Me(OEt)\cdot NH_2$, is formed when phenylhydrazoparacresetoïl is treated with moderately concentrated hydrochloric acid, and the hydrochloride produced decomposed with ammonia. It crystallises from light petroleum in slender, colourless needles, melts at 107°, and is very sparingly soluble in water, but readily in ether and alcohol; its azo-derivatives dye unmordanted cotton, but not so readily as the corresponding benzidine derivatives.

Orthotolylazoparacresol, $C_{14}H_{14}N_2O$, forms red needles with a blue reflex, melts at 98°, and is soluble in alcohol and chloroform, but insoluble in water and dilute alkalis. The *ethyl* derivative, $C_{16}H_{18}N_2O$, crystallises in red prisms with a blue reflex, melts at 82—83°, and resembles the preceding compound in its behaviour with solvents. The *hydrazo*-compound, $C_{16}H_{20}N_2O$, prepared by reducing the ethyl derivative with hydrogen sulphide in ammoniacal alcoholic solution, crystallises in colourless plates, melts at 138°, and is insoluble in water, but soluble in alcohol.

Dimethylethoxybenzidine, $NH_2\cdot C_6H_3Me\cdot C_6H_3Me(OEt)\cdot NH_2$, is formed, together with a small quantity of the azo-compound, when the hydrazo-compound just described is treated with hot dilute sulphuric acid; it crystallises from dilute alcohol in colourless needles, melts at 75°, and is readily soluble in alcohol, ether, and chloroform, but only sparingly in water; it yields coloured azo-compounds which dye unmordanted cotton fibre.

Paratolylazoparacresetoïl, $C_{16}H_{18}N_2O$, crystallises from alcohol in red needles, melts at 171°, and is readily soluble in ether and benzene. The corresponding *hydrazo*-compound, $C_{16}H_{20}N_2O$, forms colourless needles, melts at 153°, and is insoluble in water, but soluble in alcohol, benzene, &c.; when treated with hydrochloric acid, it yields a base which is analogous to diphenyline, and from which azo-compounds, having only a very feeble colouring power, are obtained.

F. S. K.

Orthonitrophenylcinnamic Acid and Phenylhydrocarbostyril. By A. OGLIALORO and E. ROSINI (*Gazzetta*, **20**, 396—402).—*Orthonitrophenylcinnamic acid*, $C_{15}H_{11}NO_4$, is prepared by heating a mixture of dry sodium phenylacetate (1 mol.), orthonitrobenzaldehyde (1 mol.), and acetic anhydride (4 mols.) for six hours at 160°. The impure acid obtained is partially purified and then converted into the *barium* salt, $(C_{15}H_{11}NO_4)_2Ba,5H_2O$, which crystallises in tufts of pale-yellow needles. The pure acid crystallises in small, pale-yellow prisms, begins to soften at 192°, and melts at 195—196°. It is sparingly soluble in water, but freely in hot alcohol; it also dissolves in ether and in benzene. From some of the alcoholic solutions obtained in the preparation of this acid, another barium salt may be obtained containing 8 mols. H_2O.

On reducing a diluted alcoholic solution of the acid with sodium amalgam, the product consists of a mixture of several substances which may be separated by fractional solution in water, dilute and absolute alcohol. The portion extracted by dilute alcohol crystallises in yellowish needles, melts at 173—174°, and has the composition of *phenylhydrocarbostyril*, $C_{15}H_{13}NO$. It is very soluble in hot alcohol, moderately in chloroform and benzene, but only sparingly in ether and light petroleum. Attempts made to prepare hydrophenylindole from this compound by fusing it with potash were unsuccessful.

S. B. A. A.

Naphthyl Methyl Ketones. By A. CLAUS and H. TERSTEEGEN (*J. pr. Chem.* [2], **42**, 517—519).—The crystals obtained by prolonged cooling of α-naphthyl methyl ketone below 0° (Abstr., 1887, 271) are β-naphthyl methyl ketone.

β-Naphthyl methyl ketone is best obtained by acetylising naphthalene in the cold and with exclusion of direct sunlight; the process is slow and the yield poor; it is freed from the α-ketone by crystallisation and pressure; it sublimes with steam in small, transparent leaflets, melts at 51·5—52° (uncorr.), boils undecomposed at 301—303° (uncorr.), and dissolves freely in alcohol, ether, and chloroform. The *oxime* forms colourless crystals which melt at 145° (uncorr.), and the *acetyl compound* of this melts at 134°. The *phenylhydrazide* melts at 171° (uncorr.).

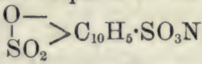
α-Naphthyl methyl acetoxime melts at 114°, and α-naphthyl methyl ketone hydrazide at 146° (uncorr.; compare Abstr., 1887, 271).

β-Naphthylglyoxylic (*β-naphthoylformic*) *acid*, obtained by oxidising the ketone with potassium permanganate, is a greenish-yellow oil which slowly crystallises and melts at 75° (?); it is pretty freely soluble in water; the *barium salt* is anhydrous; the *potassium* and *calcium salts* crystallise with 1 mol. H_2O. By reduction, it yields *β-naphthylglycollic acid*, which crystallises in small needles, sublimes in long needles, and melts at 176° (uncorr.); it is little soluble in water; its *barium salt* is anhydrous. α-Naphthylglycollic acid melts at 163° (uncorr.).

β-Naphthylacetic acid is obtained by reducing the glycollic acid with hydriodic acid; it crystallises in lustrous, silvery leaflets which melt at 142° (uncorr.); its *amide* melts at 200° (uncorr.). A. G. B.

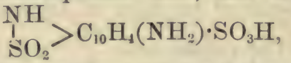
Naphthasultonsulphonic Acids and α-Naphtholsulphonamidosulphonic Acids. By A. BERNTHSEN (*Ber.*, **23**, 3088—3096).—When naphthasultone, the "naphtholsulphonic acid-S." of the Schöllkopf Aniline and Chemical Co.'s Germ. Pat. 40571, is sulphonated with concentrated sulphuric acid, and the melt poured into water, α-naphthol-δ-disulphonic acid ("S. acid" [$OH : SO_3H : SO_3H = 1 : 4 : 1'$]) is obtained (Schöllkopf Co., *loc. cit.*). The author finds that this acid is not the immediate product of sulphonation, but results from hydration of the initially-formed naphthasultonsulphonic acid-δ.

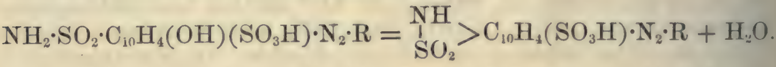
Naphthasultonsulphonic acid δ is obtained as sodium salt when 1 part of naphthasultone is gradually stirred into 8 parts of cooled 5 per cent. anhydrosulphuric acid, left for about an hour until a portion is found to be completely soluble in water, and then stirred into an externally-cooled mixture of 12 parts of ice and 16 parts of saturated brine. The *sodium* salt,



$\begin{matrix}O-\\|\\SO_2\end{matrix}>C_{10}H_5\cdot SO_3Na + 3H_2O$, which separates after some time, crystallises in thin scales or tables, is much more soluble in water than the sodium salt of naphthasultonsulphonic acid ε (Abstr., 1890, 387), and in aqueous solution gives no colour reaction with ferric chloride. On treatment with alkalis or alkaline carbonates, or by boiling with dilute (5 per cent.) sulphuric acid, or prolonged boiling with water, it is converted into sodium 1 : 4 : 1'-α-naphtholdisulphonate, whilst the latter, on treatment with suitable dehydrating agents, such as concentrated sulphuric acid at 100°, yields the naphthasultonsulphonate. The solution in concentrated ammonia, on addition of hydrochloric acid, gives a precipitate of the *sodium* salt of *naphtholsulphonamidosulphonic acid δ*, $OH\cdot C_{10}H_5(SO_2\cdot NH_2)\cdot SO_3Na + 2H_2O$, which crystallises in rhomb-like scales or plates, resembles the ε-compound (*loc. cit.*) in properties, and forms similar azo-dyes.

The azo-dyes obtained from the salts of naphtholsulphonamidosulphonic acid ε give much bluer or redder shades, are less soluble in water, and crystallise better than those from α-naphtholdisulphonic acid ε. The dyes formed by the action of diazotised xylidine, α-naphthylamine, and benzidine give respectively very blue-claret, wine-red, and bluish-violet shades, are scarcely affected by acids, and, on reduction with stannous chloride and hydrochloric acid, yield the sodium hydrogen salt of an *amidonaphtholdisulphonic acid* (probably $OH : NH_2 : SO_3H : SO_3H = 1 : 2 : 3 : 1'$).

The azo-dyes obtained with diazotised xylidine dissolve in concentrated sulphuric acid with a magenta colour, which, after a short time, changes to yellow; a corresponding colour-change occurs also with the other dyes named, and is due to hydrolysis of the $SO_2\cdot NH_2$ radicle with the production of ammonia and the corresponding azo-colouring matters derived from α-naphtholdisulphonic acid ε. A more remarkable change is that brought about by alkalis. The bluish-red azo-dye obtained with diazotised xylidine, when warmed for a short time with alkalis or alkaline carbonates, changes colour to a bright reddish-yellow, and a corresponding change to yellow or red shades ensues under like conditions with the other dye stuffs named. The azo-dyes formed can be salted out from solution, and, unlike the parent colours, are very sensitive towards acids, changing colour to blue or violet, and thus resemble many of the amidoazo-dyes. Moreover, they crystallise well, are very soluble in water containing some alkali, and in an acid bath produce shades on wool which are distinctly bluer than those from the parent dyes. On reduction with stannous chloride and hydrochloric acid, the "altered" xylidine dye, which gives a cochineal shade on wool in an acid bath, yields a sparingly soluble compound, $C_{10}H_8N_2S_2O_5 + 2H_2O$, crystallising in long, flat needles. This compound dissolves readily in alkalis, is precipitated from the alkaline solutions by acids, and by prolonged boiling with phenanthraquinol in acetic acid solution, forms an azine. It is a derivative of, but not identical with, 1 : 2 : 3 : 1′-orthonaphthylenediaminedisulphonic acid, and is regarded by the author as the *anhydride*,  $\left.\begin{array}{c}NH\\ |\\ SO_2\end{array}\right>C_{10}H_4(NH_2)\cdot SO_3H$, of this compound, the action of alkalis on the azo-dyes obtained from naphtholsulphonamidosulphonic acid ε being represented thus:—

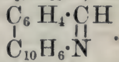


$$NH_2\cdot SO_2\cdot C_{10}H_4(OH)(SO_3H)\cdot N_2\cdot R = \left.\begin{array}{c}NH\\ |\\ SO_2\end{array}\right>C_{10}H_4(SO_3H)\cdot N_2\cdot R + H_2O.$$

Sodium hydrogen 1 : 2 : 3 : 1′-*orthonaphthylenediaminedisulphonate*, $SO_3H\cdot C_{10}H_4(NH_2)_2\cdot SO_3Na + 3H_2O$, crystallises in small needles, is much more soluble than the salt of the anhydride, and forms an azine on treatment with phenanthraquinone. W. P. W.

Dinaphthyl Picrates. By R. WEGSCHEIDER (*Ber.*, **23**, 3199—3201).—Of the dinaphthyl picrates, only the αα-compound has previously been prepared. *αβ-Dinaphthyl picrate*, $C_{20}H_{14} + C_6H_3N_3O_7$, may be readily obtained by mixing boiling alcoholic solutions of the hydrocarbon and picric acid, and crystallises in golden-yellow needles melting at 155—156°. For the preparation of *ββ-dinaphthyl picrate*, the constituents must be dissolved in boiling benzene; the salt separates out on cooling in microscopic, orange prisms, which have the composition $C_{20}H_{14},2C_6H_3N_3O_7$. The author regards the hydrocarbon obtained by Bischoff, by the action of methyl chloride on naphthalene in presence of aluminium chloride (Abstr., 1890, 1145), as probably identical with ββ-dinaphthyl. H. G. C.

Chrysidines. By A. PICTET and S. ERLICH (*Chem. Centr.*, 1890, ii, 350—351; from *Arch. sci. phys. nat., Genève* [3], **23**, 552).—The authors have pursued the investigations already commenced by Pictet (Abstr., 1890, 390), and have studied the action of heat on the two benzylidenenaphthylamines, which are obtained by heating benzaldehyde with the two naphthylamines. By passing the vapour of these compounds through a red-hot tube, two new bases, of the formula $C_{17}H_{11}N$, are obtained, the constitutional formula being, probably,



$$\begin{array}{l} C_6H_4\cdot CH \\ \,| \qquad\ \ \| \\ C_{10}H_6\cdot N \end{array}$$

. These bases, which correspond with the phenanthridines, and are similar to them in their properties, are, therefore, α- and β-chrysidine. Their alkaline solutions have a blue fluorescence, they form yellow salts with acids, and the solutions of the latter have a green fluorescence. Reduction with tin and hydrochloric acid converts them into secondary bases. α-Chrysidine melts at 108°, β-chrysidine at 126°. J. W. L.

Turpentine. By R. G. Dunwody (*Chem. Centr.*, 1890, ii, 241—242; from *Amer. J. Pharm.*, June, 1890).—The author finds very considerable variations in the specific rotatory power and the specific gravity of oil of turpentine. In 12 samples, the former varied from 2·60° to 36·64° in a 200 mm. tube, before rectification, and from 3·90° to 38·62° after rectification. The specific gravity at 15° varied from 0·856 to 0·876 before, and from 0·851 to 0·873 after rectification. The oils commenced to boil at 155—159°, and the last portions distilled between 165° and 170°; the principal part distilled at 160—162°. The author has not found Allen's test with castor-oil, for the detection of petroleum in turpentine, of much value, since an admixture of 65 per cent. of the former escaped detection by means of this test. In pure glacial acetic acid both petroleum and turpentine are perfectly miscible, but of acetic acid containing 1 per cent. of water, more and more is required for complete solution, the greater the proportion of petroleum which is present, as is shown in the following table:—

Petroleum	1	2	3	4	5	7	8 c.c.
Oil of turpentine......	9	8	7	6	5	3	2 „
Acetic acid + 1 per cent H_2O	40	60	80	110	150	230	270 „

From the pitch remaining in the retort, after the distillation of the turpentine, the author has separated, with light petroleum, two well crystallised substances, the one being abietic acid, melting at 131°, and the other, a new substance, having the composition 72—72·8 per cent. carbon, 9·75—9·50 per cent. hydrogen, 18·25—17·70 per cent. oxygen; and melting at 125—126°. J. W. L.

Terpenes and Ethereal Oils. By O. Wallach (*Annalen*, **259**, 309—324).—*Pinole glycol diacetate*, $C_{10}H_{16}O(OAc)_2$, is formed, together with pinole and pinole glycol, when pinole dibromide is warmed with sodium or silver acetate in glacial acetic acid solution; the product is purified by fractional distillation under a pressure of 13 mm. It crystallises well from water, and melts at 97—98°.

Pinole glycol, $C_{10}H_{16}O(OH)_2$, can be prepared by boiling the diacetate with very dilute sulphuric acid, or by treating the bromide with freshly precipitated silver oxide; it crystallises from light petroleum in needles, melts at 125°, is very readily soluble in chloroform, and is converted into the diacetate by boiling acetic anhydride.

Pinole hydrate, $C_{10}H_{18}O_2$, is obtained, together with cymene, when a well-cooled glacial acetic acid solution of crude pinole is saturated with hydrogen bromide, and then shaken with very dilute soda in the cold, in order to decompose the additive product; after separating the cymene by distilling with steam, the hydrate is extracted from the alkaline solution by shaking with ether. Pinole hydrate crystallises in needles or plates, melts at 131°, and is moderately easily soluble (1 in 30 at 15°) in water, but more readily in alcohol; it crystallises unchanged from boiling glacial acetic acid, but when warmed with dilute sulphuric acid, it is converted into pure pinole. It is identical with the crystalline substance which was formed, as was first observed by Sobrero (*Annalen*, **80**, 106), when oil of turpentine is exposed to direct sunlight in presence of oxygen (compare Armstrong, Proc., 1890, 99). Pinole, on oxidation with potassium permanganate, yields terebic acid and considerable quantities of oxalic acid and carbonic acid; pinole hydrate, under the same conditions, gives terpenylic acid, carbonic acid, and oxalic acid; pinole glycol seems to give the same oxidation products as the hydrate.

Pure pinole is easily prepared by boiling a benzene solution of pinole dibromide with the theoretical quantity of sodium, in the form of fine wire, until decomposition is complete; the filtered solution is evaporated, and the residual pinole purified by fractional distillation.

Pinole tribromide, $C_{10}H_{15}OBr_3$, is obtained in small quantities in the preparation of the dibromide from crude pinole; it crystallises from ethyl acetate in needles, and melts at 160° with decomposition.

F. S. K.

Fenchole, an Isomeride of Camphor. By O. WALLACH and F. HARTMANN (*Annalen*, **259**, 324—331).—A liquid of sp. gr. 0·934, possessing a strong odour of camphor, and boiling at 190—193°, can be isolated from oil of fennel; it has the composition $C_{10}H_{16}O$, and is named by the authors *fenchole*. The whole chemical behaviour of fenchole is that of a position-isomeride of camphor, as will be seen from the experiments described below; it combines with bromine in well-cooled light petroleum solution, yielding a bright-red, crystalline, unstable additive product, which is reconverted into fenchole on treatment with soda; it also yields with sodium, a solid compound, which seems to be converted into an acid by carbonic anhydride.

Fenchole oxime, $C_{10}H_{16}{:}N{\cdot}OH$, crystallises from alcohol in slender needles, and from ethyl acetate in well-defined crystals. $a : b : c = 1·3047 : 1 : 0·55259$, $\beta = 76° 20'$, which melt at 148—149°, and are very like those of camphor oxime in appearance. The *hydrochloride*, $C_{10}H_{17}NO,HCl$, melts at 118—119°, and is decomposed by alcohol. The *anhydride*, $C_{10}H_{15}N$, prepared by dissolving the oxime in dilute sulphuric acid, is a colourless liquid, boiling at 217—219°; it can be distinguished from the anhydride of camphor oxime by the fact that it yields a crystalline *hydrobromide*, $C_{10}H_{15}N,HBr$, which is, however, very unstable.

Isofenchole oxime, $C_{10}H_{17}NO$, is formed when fenchole oxime anhydride is boiled with alcoholic potash for five to six hours; it crystallises from alcohol in plates, melts at 113—114°, and is readily soluble in alcohol, ether, and acids, and moderately soluble in water.

Fencholenic acid, $C_{10}H_{16}O_2$, is obtained when isofenchole oxime is boiled with alcoholic potash for four days, but some of the oxime remains unchanged. It is an almost colourless liquid, boils at 257—260°, and forms a sparingly soluble silver salt and a deliquescent ammonium salt. F. S. K.

Rose-oil. By V. MARKOVNIKOFF (*Ber.*, **23**, 3191).—Rose-oil consists, as is well known, of liquid constituents and stearoptene. The latter melts at 36·5°, and has all the properties of a paraffin; it is perfectly inodorous, and is, therefore, of no value with regard to the quality of the oil. The liquid portion or eleoptene boils within narrow limits, and appears to be a mixture of two substances, $C_{10}H_{20}O$ and $C_{10}H_{18}O$, one of which is an alcohol, and forms the chief constituent of rose-oil. H. G. C.

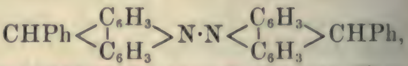
β-Methylpyridine. By C. STOEHR (*Ber.*, **23**, 3151—3157).—The product obtained by the distillation of strychnine or of brucine is not homogeneous. After purification, however, it yields β-methylpyridine, which boils at 142—143°, and is identical with the synthetical product from glycerol, acetamide, and phosphoric anhydride. The mercurochloride melts at 145—146°, the platinosochloride at 257—257·5°, and the platinochloride at 201—202°. Ladenburg (Abstr., 1890, 1432) gives three melting points for this last compound (from synthetical β-methylpyridine), which range between 191° and 198°, and it is suggested that he had to deal with varying mixtures of the two platinum compounds. Ladenburg's theory of the constitution of pyridine, so far as it is based on the existence of two β-methyl derivatives, is thus proved to be erroneous. J. B. T.

A New Class of Acridines: Phenylcarbazacridine. By D. BIZZARRI (*Gazzetta*, **20**, 407—417).—*Phenylcarbazacridine*, $C_{19}H_{11}N$, is formed when a mixture of pure carbazole (20 grams) with benzoic acid (15 grams) and fused zinc chloride (45 grams) is heated for five hours at 120—130°, and the alcoholic solution of the product precipitated with strong aqueous ammonia. The product when pure crystallises from alcohol in minute, white scales, turns green on heating to 150°, and melts at 186·5°. It dissolves in most of the ordinary solvents, but only sparingly in absolute alcohol, and not at all in water. It crystallises from benzene in groups of rectangular laminæ, and from xylene in peculiar, spherical tufts. With acetic acid, it forms an intense green solution, which is dichroic when concentrated (0·25 per cent.), appearing emerald-green by reflected, and garnet-red by transmitted light. It is not affected by boiling with alkalis, and only partially decomposed by heating with soda-lime. It is dissolved by benzoic chloride, but not further affected.

The *methiodide*, $C_{19}H_{11}N,MeI$, prepared by heating the base with methyl iodide at 140°, crystallises in brownish-yellow plates, soluble in alcohol and acetic acid. From these solutions, the base is reprecipitated on the addition of water. Boiling alcoholic potash decomposes it into the free base, methyl alcohol, and potassium iodide. On gently heating, it is similarly split up into the base and methyl iodide.

The *hydrochloride* forms emerald-green scales, soluble in acetic acid and in alcohol, but not in water. It dissociates even in alcoholic solution, and is only stable in presence of an excess of free hydrochloric acid. It is completely decomposed by boiling water. The *sulphate* forms a green, shining mass, soluble in acetic acid and in alcohol, but not in water. It is gradually decomposed by boiling water, and the alcoholic solution is unstable in the absence of free sulphuric acid. The *picrate* and *hydriodide* crystallise in green plates decomposed by water, and forming unstable alcoholic solutions. The *chromate* crystallises in scales decomposed by water and alcohol.

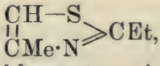
Benzoylcarbazole, $C_{19}H_{13}NO$, is obtained by heating carbazole with benzoic anhydride at 240°. It crystallises from alcohol in white, acicular prisms, melts at 95·5°, dissolves in benzene, ether, &c., but only sparingly in alcohol. It is decomposed by alcoholic potash into carbazole and benzoic acid. Its formation and decomposition, together with the analogy to acetylcarbazole, establish for this compound the constitution $C_{12}H_8NBz$. On heating it with zinc chloride at 130—150°, phenylcarbazacridine is formed.

Phenylhydrocarbazacridine,  $\mathrm{CHPh}<\begin{matrix}C_6H_3\\|\\C_6H_3\end{matrix}>N\cdot N<\begin{matrix}C_6H_3\\|\\C_6H_3\end{matrix}>\mathrm{CHPh}$, prepared by reducing phenylcarbazacridine with zinc-dust, crystallises in yellowish leaves which turn brown and melt at 172°, and dissolves in acetic acid, alcohol, and ether, but not in water. It reduces silver nitrate in alcoholic solution, and picric acid imparts to it an orange coloration. It has no basic properties, but acids and potassium permanganate convert it into phenylcarbazacridine.

When carbazole is heated with benzoic acid and zinc chloride at 150—160°, there is formed, besides the acridine described and resinous products, a compound of unknown constitution, which crystallises from boiling alcohol in tables which melt at 210°, and are stained yellow by picric acid. At 200—210°, no phenylcarbazacridine is formed, the products consisting mainly of resins. At 280°, the mass is gradually carbonised.

S. B. A. A.

Thiazoles. By K. HUBACHER (*Annalen*, **259**, 228—253; compare Hantzsch, Abstr., 1889, 413, 723, and 1890, 1238).—*Thiopropionamide*, C_3H_7NS, can be prepared by treating propionamide with phosphorus pentasulphide, as described by Hantzsch (*loc. cit.*) in the case of thiacetamide; the yield is, at the most, 10 per cent. of the amide employed. It crystallises in yellowish plates, melts at 42—43°, and is very readily soluble in benzene, but only sparingly in ether, alcohol, and water.

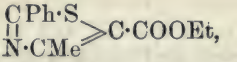
α-Methyl-μ-ethylthiazole,  $\begin{matrix}CH-S\\ \| \\ CMe\cdot N\end{matrix}>CEt$, is obtained when thiopropionamide is treated with chloracetone in alcoholic solution, and the product decomposed with soda. It is a colourless liquid, boils at 159·5—160° (728·5 mm.), has an odour of pyridine, and is miscible with alcohol and ether, but is only sparingly soluble in cold water. The *platinochloride*, $(C_6H_9NS)_2,H_2PtCl_6$, forms small, yellowish-red crystals, and melts at 177° with decomposition.

α-Phenyl-μ-ethylthiazole, $C_{11}H_{11}NS$, is formed when thiopropionamide is treated with bromacetophenone in like manner; the product is dissolved in dilute hydrobromic acid, and the crystalline hydrobromide, which is deposited from the filtered solution, decomposed with soda. The base is a colourless oil, of agreeable odour, boils at 295° (729 mm.), and is insoluble in water, but miscible with alcohol and ether. The platinochloride, $(C_{11}H_{11}NS)_2,H_2PtCl_6$, forms light-yellow, microscopic crystals, and melts at 128—129° with decomposition. The *hydrobromide*, $C_{11}H_{11}NS,HBr$, crystallises in colourless needles, melts at 68—70°, and is decomposed by cold water or when kept over sulphuric acid.

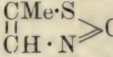
μ-Phenylthiazole, C_9H_7NS, is formed when thiobenzamide is heated at 100° for several hours with dichlorether and sodium acetate in alcoholic solution; the dark, resinous product is extracted with dilute hydrochloric acid, the base liberated with soda, and distilled. It is a colourless oil boiling at 266—268° (732 mm.). The *hydrochloride*, $C_9H_7NS,HCl + 2H_2O$, crystallises from dilute hydrochloric acid in plates, melts at 61—62°, loses its water over sulphuric acid, and is immediately decomposed by water. The *platinochloride*, $(C_9H_7NS)_2,H_2PtCl_6 + 2H_2O$, is a yellow, crystalline compound melting at 173—175° with decomposition; it loses its water at 110°. The picrate crystallises in yellow needles, melts at 124—125°, and is only very sparingly soluble in water, but readily in hot alcohol.

α-Methyl-μ-phenylthiazole, $C_{10}H_9NS$, prepared by treating thiobenzamide with chloracetone in alcoholic solution, is an oil boiling at 277·5—278° (724 mm.).

αμ-Diphenylthiazole, $C_{15}H_{11}NS$, obtained from thiobenzamide and bromacetophenone in like manner, crystallises from alcohol in colourless plates, melts at 92—93°, boils above 360° without decomposition, and is readily soluble in alcohol and ether; it is a very feeble base, but its salts are unstable and cannot be obtained in a pure condition.

Ethyl α-methyl-μ-phenylthiazolecarboxylate,  $\begin{matrix}\mathrm{CPh{\cdot}S}\\ \| \\ \mathrm{N{\cdot}CMe}\end{matrix}\!>\mathrm{C{\cdot}COOEt}$, is obtained when thiobenzamide is warmed with ethyl chloracetoacetate, and the salt thus produced decomposed with soda; it crystallises from ether in yellow needles, and melts at 43°. The corresponding acid, $C_{11}H_9NS$, prepared by hydrolysing the ethereal salt with alcoholic potash, crystallises in colourless needles, melts at 202—204·5°, and, when heated more strongly, sublimes in long needles, being at the same time partially decomposed into carbonic anhydride and methylphenylthiazole. It is readily soluble in alcohol, but only sparingly in ether, and almost insoluble in water; in its neutral solutions many metallic salts produce a precipitation.

A mixture of various compounds, which contains α-chloropropaldehyde, can be obtained by gradually adding sulphuryl chloride to an ethereal solution of propaldehyde in which barium carbonate is suspended; the ethereal solution is washed with water and sodium carbonate consecutively, dried, and then submitted to fractional distillation; the portion passing over between 60° and 150° was employed in some of the experiments described below.

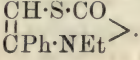
βμ-Dimethylthiazole,  $\begin{array}{l}\text{CMe}\cdot\text{S}\\ \|\\ \text{CH}\cdot\text{N}\end{array}\!\!\geqslant\text{CMe}$, is formed in small quantities when crude α-chloropropaldehyde is warmed with thiacetamide, the product boiled with hydrochloric acid, and then treated with soda; it is purified by distilling with steam, and then submitted to fractional distillation. It is a colourless liquid, boils at 148—150° (734 mm.), and is sparingly soluble in water, but readily in ether and alcohol. The *platinochloride*, $(C_5H_7NS)_2,H_2PtCl_6$, crystallises in prisms and melts at 202°; the picrate crystallises in small, yellow needles, melts at 166—167°, and is sparingly soluble in water.

β-Methyl-μ-amidothiazole, $C_4H_6N_2S$, is obtained by heating crude α-chloropropaldehyde with thiocarbamide; it crystallises from water in yellowish plates, melts at 94—95°, and is readily soluble in alcohol, but less readily in ether, and only sparingly in cold water. The *platinochloride* forms nodular, crystalline aggregates, and melts at 181—182° with decomposition.

αβ-Diphenyl-μ-amidothiazole, $C_{15}H_{12}N_2S$, can be prepared by warming bromodeoxybenzoïn with thiocarbamide and decomposing the product with dilute sodium carbonate. It crystallises from alcohol in yellowish needles, melts at 185—186°, and is readily soluble in alcohol, but only sparingly in ether, and insoluble in water. The *hydrobromide*, $C_{15}H_{21}N_2S,HBr$, crystallises in needles, melts at 215—217° with partial decomposition, and is only sparingly soluble in dilute hydrobromic acid.

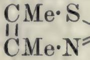
αβ-Diphenyl-μ-methylthiazole, $C_{16}H_{13}NS$, can be obtained by treating an alcoholic solution of thiacetamide with bromodeoxybenzoïn; it is purified by means of the hydrochloride, a crystalline compound melting at 96—97°. The base crystallises in colourless needles, melts at 51—52°, and is insoluble in water, but readily soluble in alcohol and ether.

Triphenylthiazole, $C_{21}H_{15}NS$, prepared from thiobenzamide and bromodeoxybenzoïn, crystallises in colourless, well-defined prisms, melts at 86—87°, and is readily soluble in ether, but more sparingly in alcohol, and insoluble in water. It crystallises unchanged from hot concentrated hydrochloric acid, in which it is only very sparingly soluble.

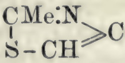
Phenylhydroxythiazole (m. p. 204°) is formed when bromacetophenone is treated with xanthogenamide under various conditions. The *ethyl* derivative of phenyloxypseudothiazole is obtained when phenylhydroxythiazole is treated with sodium ethoxide and ethyl iodide at 140—150°. It crystallises from ether in colourless plates, melts at 71°, and is decomposed by concentrated hydrochloric acid at 220° yielding ethylamine; it has, therefore, the constitution expressed by the formula  $\begin{array}{l}\text{CH}\cdot\text{S}\cdot\text{CO}\\ \|\\ \text{CPh}\cdot\text{NEt}\end{array}\!\!>$.

F. S. K.

Trimethylthiazole, Methylethylthiazole, and Thiazolecarboxylic Acids. By T. Roubleff (*Annalen*, **259**, 253–276).—*Ethyl α-chloromethylacetoacetate*, COMe:CMeCl·COOEt, is obtained when sulphuryl chloride is gradually added to well-cooled ethyl methylacetoacetate. It is a colourless liquid of sp. gr. 1·0591 at 16·5°, with a pleasant, rather pungent odour, and boils at 192—194° (corr.). It does not yield a salt with copper acetate under any conditions; the corresponding bromo-compound, obtained by brominating ethyl methylacetoacetate, gives a copper salt, and can be readily converted into thiazole derivatives. It is evident, therefore, that chlorine and bromine, at the ordinary temperature, displace different hydrogen atoms in ethyl methylacetoacetate (compare Hantzsch, Abstr., 1890, 1238; it has, however, been stated by Genvresse (*Compt. rend.*, **107**, 187) that both α- and γ-chloro-derivatives are formed when ethyl acetoacetate is treated with chlorine at 170°.

Trimethylthiazole,  $\begin{matrix}\mathrm{CMe{\cdot}S}\\ \| \\ \mathrm{CMe{\cdot}N}\end{matrix}\!>\!\mathrm{CMe}$, is formed when crude methyl chlorethyl ketone, prepared by hydrolysing ethyl α-chlormethylacetoacetate with 40 per cent. hydrochloric acid, or by chlorinating methyl ethyl ketone with sulphuryl chloride, is warmed with thiacetamide; the product is boiled with dilute hydrochloric acid, the filtered solution mixed with soda, and the precipitated oil extracted with ether. Trimethylthiazole can also be obtained by brominating methyl ethyl ketone in ethereal solution, and treating the methyl bromethyl ketone produced with thiacetamide. It is a colourless liquid of sp. gr. 1·0130 at 16°, boils at 166·5—167·5° (corr.), and is moderately easily soluble in cold water. The *platinochloride*, $(C_6H_9NS)_2,H_2PtCl_6$, crystallises in orange prisms, and melts at 232—233° with decomposition. The *hydrochloride* is a crystalline, deliquescent compound melting at 173—174°. The *aurochloride* is sparingly soluble in boiling water, from which it crystallises in yellow needles melting at 155—156°. The *picrate* crystallises from hot water in yellow prisms melting at 133°, and the *mercurochloride* crystallises in small plates melting at 118—119°.

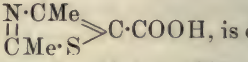
Ethyl bromomethylacetoacetate, $CH_2Br{\cdot}CO{\cdot}CHMe{\cdot}COOEt$, prepared by brominating ethyl methylacetoacetate, is an oil of sp. gr. 1·1981 at 16·5°, with a disagreeable, pungent odour; its alcoholic solution gives a reddish-violet coloration with ferric chloride, and a green, crystalline precipitate with copper acetate.

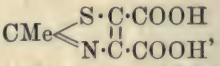
Ethyl methylthiazolepropionate,  $\begin{matrix}\mathrm{CMe{:}N}\\ | \\ \mathrm{S{-}CH}\end{matrix}\!>\!\mathrm{C{\cdot}CHMe{\cdot}COOEt}$, is formed when thiacetamide is treated with ethyl bromomethylacetoacetate; it is a thick, dark-brown oil, and on hydrolysis with alcoholic soda, it yields an oily acid which, when distilled with lime, is converted into μ-methyl-α-ethylthiazole.

μ-Methyl-α-ethylthiazole, C_6H_9NS, purified by fractional distillation, is an oil boiling at 169—171° (corr.). The *platinochloride*,

$$(C_6H_9NS)_2,H_2PtCl_6,$$

forms reddish-yellow prisms, and melts at 182–183° with decomposition. The *picrate* crystallises from water in well-defined, lemon-yellow prisms, melting at 114—115°, and the *mercurochloride* crystallises in prisms melting at 138—139°.

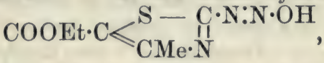
αμ-Dimethylthiazole-β-carboxylic acid,  $\begin{array}{l}N\cdot CMe\\ \| \\ CMe\cdot S\end{array}\!>C\cdot COOH$, is obtained when the ethyl salt (compare Hantzsch, Abstr., 1889, 724) is hydrolysed with alcoholic potash. It crystallises from hot water in long, colourless needles or small prisms, melts at 227° with evolution of gas, sublimes without decomposition, and is only moderately easily soluble in hot water, but more readily in alcohol and ether. The salts of the alkaline earths are readily soluble in water, but in neutral solutions of the ammonium salt, many metallic salts produce a precipitation. The *silver* salt, $C_5H_6NS\cdot COOAg$, crystallises from boiling water in colourless needles, and quickly darkens on exposure to light. The *hydrochloride*, $C_6H_7O_2NS,HCl$, crystallises from cold dilute hydrochloric acid in transparent plates, and is decomposed by water, or when heated at 70°. The acid is completely destroyed by potassium permanganate, but it is not acted on by boiling concentrated nitric acid.

μ-Methylthiazoledicarboxylic acid,  $CMe<\begin{array}{l}S\cdot C\cdot COOH\\ \qquad \| \\ N\cdot C\cdot COOH\end{array}$, can be obtained by warming ethyl chloroxalacetate, prepared by treating ethyl oxalacetate with sulphuryl chloride, with thiacetamide, and hydrolysing the product with alcoholic soda. It crystallises from warm water in long, colourless needles with 1 mol. H_2O, sublimes below 100°, melts at 169° with evolution of carbonic anhydride, and is readily soluble in cold water and alcohol, but very sparingly in ether, carbon bisulphide, benzene, &c. The *barium* salt, $C_6H_3NSO_4Ba + 2H_2O$, crystallises in colourless needles, and loses the whole of its water at 130°. The *mercury* salt, $C_6H_3NSO_4Hg + 3\frac{1}{2}H_2O$, is colourless and crystalline, and loses its water at 115°. Most of the other salts, except those of calcium, magnesium, and the alkalis, are sparingly soluble in water.

μ-Methylthiazole-β-carboxylic acid, $C_5H_5O_2NS$, is formed with evolution of carbonic anhydride, when the dicarboxylic acid just described is heated for some time at 170—172°. It crystallises from water in small, colourless needles or prisms containing 1 mol. H_2O, loses its water at 70—80°, and melts at 144—145°; it is readily soluble in cold water, but more sparingly in alcohol, ether, and chloroform, and almost insoluble in carbon bisulphide and benzene. The salts are all readily soluble, except those of silver, copper, and mercury.

Ethyl μ-amidothiazoledicarboxylate, $C_9H_{12}O_4N_2S$, is obtained in the form of the hydrochloride when ethyl chloroxalacetate is mixed with thiocarbamide; when the crystalline salt, which is only very sparingly soluble in water, is treated with potassium carbonate, the base is liberated, and can be purified by crystallisation from ether-alcohol. It forms well-defined prisms which contain $\frac{1}{2}$ mol. C_2H_6O, and melt at 90°, the alcohol-free compound melting at 112°.

μ-Amidothiazoledicarboxylic acid, $C_5H_4N_2SO_4$, prepared by hydrolysing the ethyl salt with alcoholic soda, crystallises from hot water in yellowish needles with 1 mol. H_2O, loses its water at 150°, melts at 229—230° with complete decomposition, and is only sparingly soluble in most ordinary neutral solvents. Attempts to convert this acid and its ethyl salt into αβ-thiazoledicarboxylic acid by means of nitrous acid were unsuccessful. F. S. K.

Diazo-compounds of the Thiazole Series. By M. WOHMANN (*Annalen*, **259**, 277—300).—A compound of the composition $C_7H_9N_3O_3S$, which seems from its behaviour to be the diazo-hydrate of ethyl methylthiazolecarboxylate,  $COOEt\cdot C<\begin{array}{l}S - C\cdot N{:}N\cdot OH\\ \qquad\;\; \|\\ CMe\cdot N\end{array}$, is formed when ethyl methylamidothiazolecarboxylate (10 grams), prepared as described by Zürcher (Abstr., 1889, 725), is dissolved in a mixture of 33 per cent. hydrochloric acid (30 c.c.) and water (200 c.c.), and sodium nitrite (25 grams), dissolved in water (100 c.c.), gradually added to the cooled solution; after expelling the nitrous acid with a stream of air, the precipitate is quickly separated by filtration, washed with very dilute nitric acid, alcohol, and ether consecutively, and then recrystallised from cold ether, from which it separates in small, yellowish plates. It melts and explodes at 99—100°, is rather unstable, gives Liebermann's reaction, and is moderately easily soluble in glacial acetic acid, alcohol, benzene, and light petroleum, but more sparingly in ether. In some respects, it behaves like an aromatic diazo-compound, being soluble in alkalis and cold concentrated acids, and giving dyes with phenols; in others, it behaves like a nitroso-derivative, and, when treated with most ordinary reducing agents, is reconverted into the amido-compound.

Ethyl hydrazomethylthiazolecarboxylate is obtained in an impure condition by carefully reducing the diazo-compound described above with zinc-dust and dilute ammonia. It is a crystalline, very unstable compound, which reduces Fehling's solution in the cold, and combines readily with aldehydes and ketones in acetic acid solution, yielding crystalline compounds; the condensation product obtained with acetone forms bright-yellow needles and is unstable.

Ethyl methylchlorothiazolecarboxylate, $C_7H_8O_2NSCl$, can be prepared by gradually adding the diazo-compound to warm 15 to 18 per cent. hydrochloric acid, and heating the mixture until the evolution of nitrogen ceases; the solution is then diluted with water, the product distilled with steam in order to separate it from the azimido-compound described below, and then treated with dilute hydrochloric acid to free it from ethyl methylamidothiazolecarboxylate. It crystallises from alcohol in transparent prisms, melts at 50—51°, has a sweet, sharp taste, and a fruity odour; it is soluble in concentrated hydrochloric acid and dissolves freely in most ordinary organic solvents, but is insoluble in water.

Ethyl methylbromothiazolecarboxylate, $C_7H_8O_2NSBr$, prepared by treating the diazo-compound with hydrobromic acid in a similar manner, crystallises from alcohol in large, colourless plates, melts at 70—71°, and resembles the chloro-derivative in chemical and physical properties. The corresponding *iodo*-compound, $C_7H_8O_2NSI$, is formed in small quantity when the diazo-compound is treated with 2 to 3 per cent. hydriodic acid, the principal product, however, being regenerated amido-compound; it separates from alcohol and glacial acetic acid in crystals melting at 86—87°, and resembles the chlorinated derivative very closely. The yield of the iodo-compound is only 5 to 10 per cent., whereas in the case of the chlorinated and brominated derivatives the yield is 60—70 per cent. of the ethyl methylamidothiazolecarboxylate employed.

Ethyl methylazimidothiazolecarboxylate, $C_{14}H_{17}O_4N_5S_2$, is gradually deposited in orange-red needles when the diazo-compound is boiled with alcohol or heated for a long time with almost any neutral solvent. It separates from alcohol and glacial acetic acid in crystals, melts at 224—225°, and is moderately easily soluble in benzene and light petroleum, but more sparingly in ether; it dissolves freely in mineral acids, but it is only very sparingly soluble in, and is decomposed by, alkalis. On reduction with zinc-dust and hydrochloric acid, it is converted into ethyl methylamidothiazolecarboxylate, and on hydrolysis with alcoholic potash it is converted into the corresponding *acid*, $C_{10}H_9O_4N_5S_2$, which crystallises in slender, yellowish-red needles, melts at 214° with decomposition, and is almost insoluble in all ordinary neutral solvents.

Methylchlorothiazolecarboxylic acid, $C_5H_4O_2NSCl$, is obtained when the ethyl salt described above is hydrolysed with cold alcoholic potash, but the product is always mixed with some methylhydroxythiazolecarboxylic acid, from which it can only be imperfectly separated by fractional crystallisation. It seems to melt at about 144—148°, and is very readily soluble in all organic solvents, but only moderately easily in hot water. The *silver* salt, $C_5H_3O_2NSClAg$, crystallises in colourless needles.

The *bromo*-acid, $C_5H_4O_2NSBr$, and the *iodo*-acid, $C_5H_4O_2NSI$, were also obtained in an impure condition; the former seems to melt at about 162—164°, the latter at about 174—176°, with decomposition.

Methylhydroxythiazolecarboxylic acid, $C_5H_5O_3NS$, is formed when methylchlorothiazolecarboxylic acid is heated at 170°, but it is best prepared by fusing the ethyl salt of the chlorinated acid with concentrated potash. It crystallises from alcohol in small needles, melts at 222° with decomposition, and is moderately easily soluble in alcohol and hot water, but only sparingly in ether, and almost insoluble in benzene and light petroleum. The *ammonium* salt, $C_5H_8O_3N_2S$, crystallises from water in large prisms with 3 mols. H_2O, and melts at 138° with liberation of carbonic anhydride, being transformed into methylhydroxythiazole (m. p. 102°); this hydroxy-compound is also obtained when the acid is carefully heated.

Ethyl methylthiazolecarboxylate, $C_7H_9O_2NS$, can be easily prepared by treating the chlorinated derivative with zinc-dust and acetic acid at a temperature below 50°. It crystallises in transparent prisms, melts at 27—28°, boils at 232—233° (726 mm., thermometer entirely in vapour), is volatile with steam, and is very readily soluble in all ordinary solvents except water. The corresponding *acid*, $C_5H_5O_2NS$, prepared by hydrolysing the ethyl salt with alcoholic potash, crystallises from hot water in nacreous plates, and from alcohol in small needles, melts at 257° with decomposition, and is almost insoluble in benzene and light petroleum; most of the salts of the heavy metals are insoluble. F. S. K.

Synthesis of a Diamidocarbazole from Benzidine. By E. Täuber (*Ber.*, **23**, 3266—3269).—*Diamidocarbazole sulphate*, $C_{12}H_{11}N_3,H_2SO_4$, can be obtained by heating metadiamidobenzidine hydrochloride (compare Abstr., 1890, 782) with 18 per cent. hydrochloric acid (6 parts) for 10 hours at 180—190°, and treating the filtered solution of the product with excess of hot dilute sulphuric acid; it crystallises in colourless needles and is almost insoluble in boiling water. The *base*, $C_{12}H_{11}N_3$, crystallises from hot alcohol in flat, lustrous needles, and turns black at 200°, but without melting; it is not identical with the diamidocarbazole obtained by nitrating carbazole and reducing the product (compare D. R.-P., No. 46438). The hydrochloride is moderately easily soluble in water but is precipitated from the solution in crystals on the addition of hydrochloric acid. The tetrazo-derivatives of the base dye unmordanted cotton very readily, the shades being the same as those obtained with the corresponding benzidine dyes. F. S. K.

Tritopine and other Rare Opium Bases. By E. Kauder (*Arch. Pharm.*, **228**, 419—431).—The rarer alkaloïds were sought for in large quantities of the mother liquor, obtained in the preparation of morphine, &c., on a manufacturing scale. The results largely confirm and extend those previously obtained by Hesse. After removing the relatively large quantities of morphine, codeïne, narceïne, thebaïne, papaverine, and narcotine still present in the mother liquor, a considerable amount of cryptopine was the first product. The mother liquor, diluted with water, warmed to 60°, and poured into water containing excess of sodium hydroxide, gave a dark, resinous precipitate. The filtrate, further treated with hydrochloric acid, ammonia, &c., gave only narcotine and laudanine. Lanthopine and codamine were not detected. Laudanine, whilst soluble in sodium hydroxide, can also be methylated, so that it ranges with morphine. The methyl ether of laudanine, melting at 113°, is not identical with laudanosine. The dark, resinous precipitate above described was dissolved in a little alcohol, treated with ether until precipitation ceased, the ether filtered off, and treated with acetic acid water. Excess of potassium iodide added to this solution precipitates almost the whole of the alkaloïds, with much resin. After 24 hours, the mother liquor was poured off, the residue mixed with a little alcohol and set aside for several days. Large quantities of iodides thus crystallised out, which were pressed and washed with a little alcohol. No more crystals could be obtained from the tenacious mother liquor containing most of the resin. The iodides were converted into the free bases, and these dissolved in hydrochloric acid and concentrated. After the addition of an equal volume of alcohol and then alcoholic ammonia, crystals of protopine, and a new base, tritopine, separated. The filtrate from these was treated with much ether, the ether agitated with oxalic acid water, the aqueous solution concentrated and treated with more oxalic acid.

After 24 hours, a few hard crystals of protopine and cryptopine binoxalate had formed. Further treatment of the mother liquor with potassium iodide, &c., separated small quantities of cryptopine, protopine, and tritopine, whilst still further concentration yielded laudanosine, easily purified by crystallising from light petroleum. *Tritopine*, $C_{42}H_{54}N_2O_7$, melts at 182°. It is easily soluble in chloroform, slightly in ether; 1 part dissolves in 40 parts of boiling alcohol, from which it crystallises in transparent prisms. Several salts of this base are described. The relative amounts of the bases found were approximately, laudanosine, 1; tritopine, 2; protopine, 3·5; laudanine, 20; cryptopine, 70.

J. T.

Atropamine. By O. HESSE (*Chem. Centr.*, 1890, ii, 446—447; from *Pharm. Zeit.*, **35**, 471).—The author has separated an alkaloïd from the roots of *Atropa belladonna*, which he has named *atropamine*. At ordinary temperatures, it is solid, but is quite liquid at 60°. It is precipitated from solutions of its salts by potash or soda as an oil; it is readily soluble in alcohol, ether, and chloroform. It has the formula $C_{17}H_{21}NO_2$; it contains 1 mol. H_2O less than atropine, hyoscyamine, and hyoscine, and is isomeric with belladonnine. It forms haloid salts, which crystallise very beautifully; this distinguishes it from belladonnine and other atropa alkaloïds.

It is optically inactive. A 2 per cent. solution of the hydrochloride has, according to Berlin, no mydriatic action. Protracted boiling with alcoholic solution of barium hydroxide causes a decomposition with formation of tropine and an acid which is neither tropic, atropic, nor isatropic acid. By the action of hydrochloric acid, atropamine is converted into belladonnine, and is then further transformed as by heating with alcoholic barium hydroxide. Atropamine is very readily decomposed by acids, and hence it has been overlooked in the past. The acid above referred to, the nature of which has not been determined, sometimes causes a smell of bitter almond oil if mixed with potassium permanganate, a reaction which is not produced with atropamine.

J. W. L.

Root Constituents of Scopolia atropoïdes. By E. SCHMIDT (*Arch. Pharm.*, **228**, 435—441). A new investigation, in which the bases were precipitated as aurochlorides, yielded hyoscyamine, but only a very small amount of atropine, and a minute quantity of aurochloride, which agreed as to its melting point, 198—199°, and analysis with the hyoscine compound. Scopoletin has been proved to be identical with methylæsculetin by Takahashi (Abstr., 1889, 255). F. Schmidt has found by the application of Zeisel's method (heating with hydriodic acid, &c.) that scopoletin contains only one methoxyl group. The æsculetin produced by this reaction was isolated and analysed. The methylæsculetin of Tiemann and Will melts at 184°, whilst scopoletin melts at 199—200°, so that one is probably the α- and the other the β-methylæsculetin; but which is which has not been determined.

J. T.

Alkaloïds of Chelidonium majus. By F. Selle (*Arch. Pharm.*, **228**, 441—462).—Besides the two alkaloïds chelidonine and chelerythrine, E. Schmidt found strong evidence of the presence of *α-homochelidonine*, *β-homochelidonine*, and a third base seemingly identical with *protopine*, an alkaloïd obtained by Hesse from opium. The author has separated and investigated these three new bases. The following general method is used to extract the bases from the root of the plant. The dried and pulverised material is repeatedly extracted with alcohol containing acetic acid; after filtration and dilution with water, the alcohol is distilled off and the resin separated is removed by another filtration. The filtrate is treated with ammonia and shaken up with chloroform; the chloroform solution on evaporation leaves a residue which is dissolved in the least possible amount of alcohol containing hydrochloric acid. After cooling, the alcoholic solution is separated by filtration from the undissolved and crystalline portion, consisting of chelidonine and protopine hydrochlorides. The alcoholic solution is diluted with water, freed from alcohol, strongly diluted with hydrochloric acid water, filtered, and treated with ammonia in excess. The filtrate contains β-homochelidonine, which may be extracted by shaking up with alcohol. The precipitate contains α-homochelidonine and chelerythrine; the latter can be obtained by long digestion with ether.

β-Homochelidonine, $C_{19}H_{15}(OMe)_2NO_3$, appears as well formed, colourless, seemingly monoclinic crystals, which melt at 159°. A solution (1 : 100) gives a white precipitate with mercury chloride, phosphotungstic acid, and potassium cadmium iodide; yellowish-white with potassium mercury iodide and phosphomolybdic acid; yellow with bromine-water; reddish-yellow with potassium bismuthoiodide. Concentrated sulphuric acid gives a beautiful violet coloration. Froehde's reagent yields a transient yellow, violet, and green coloration. which becomes a beautiful blue, and finally an intense moss-green. Erdman's reagent gives a yellow, passing quickly to a beautiful violet, which gradually becomes dirty-violet. Concentrated nitric acid produces a yellow colour. Vanadium sulphuric acid gives yellow, violet, and intense blue; after a time this become green. The alkaloïd is easily soluble in hydrochloric, sulphuric, nitric, and acetic acids. The hydrochloride, platinochloride, and aurochloride are described.

α-Homochelidonine, $C_{19}H_{15}(OMe)_2NO_3$, forms large, rhombic crystals, when recrystallised from its solution in ethyl acetate, which melt at 182°. Its solution (1 : 100) yields precipitates similar to those given by the β-base, with the addition that tannin gives a white precipitate, soluble in excess. Concentrated sulphuric acid dissolves the base, with the gradual formation of pale-yellow streaks. Concentrated nitric acid gives a yellow coloration. Froehde's reagent produces a dirty brownish-green and then brownish-yellow tint. Erdmann's reagent and vanadium sulphuric acid yield a reddish-yellow coloration. The hydrochloride, platinochloride, and aurochloride are described and analysed.

Protopine (?) was finally obtained in colourless crystals from its solution in a mixture of much chloroform with little ethyl acetate; its melting point is 207°. The amount obtained was insufficient to admit of a determination of its formula, but $C_{20}H_{17}NO_5$ is indicated, and Zeisel's method does not indicate the presence of methoxyl groups. Its reactions with precipitants are the same as those given for α-homochelidonine. J. T.

Alkaloïds of the Rhizome of Veratrum album. By G. Salzberger (*Arch. Pharm.*, **228**, 462—483).—Besides the three crystallisable bases, jervine, rubijervine, and pseudojervine already known, the author has isolated two new ones, *protoveratrine*, an extremely powerful poison, and *protoveratridine*. Two methods of extraction were followed: one, the baryta method, is relatively rapid, and gives jervine, rubijervine, and protoveratridine, but no protoveratrine; the other, the metaphosphoric acid method, yields protoveratrine and pseudojervine, with small amounts of jervine and rubijervine. The yield varies considerably, and the method of drying the rhizome is not without influence on the result. The moderately pulverised rhizome was mixed with barium hydroxide and water, and extracted with ether. The extract was freed from ether at the lowest possible temperature in a gentle current of hydrogen. The dark-green syrup thus obtained gave a crop of crystals mainly consisting of jervine. Recrystallisation from alcohol separated a little protoveratridine, and further treatment by Wright and Luff's process with dilute sulphuric acid yielded a small amount of rubijervine. The mother liquor from the crude jervine by further treatment yielded a little more protoveratridine and rubijervine, and other uncrystallisable and decomposition products. Protoveratrine can be easily extracted from the drug by cold water, but cannot be obtained in a crystalline form by this means. To obtain the crystalline base, the rhizome is freed from fatty and resinous compounds by treatment with ether, and an alcoholic extract of the residue is prepared. This extract is freed from alcohol in a vacuum, mixed with much acetic acid water, quickly filtered from the insoluble residue, and treated with solid metaphosphoric acid, until no further precipitate appears. The voluminous precipitate contains much amorphous matter, besides insoluble compounds of jervine and rubijervine. The filtrate is treated with excess of ammonia, filtered, and shaken up with ether, and from the ether extract the protoveratrine crystallises out when the ether is distilled off. By recrystallisation from strong alcohol, the base is purified and separated from some little remaining rubijervine and jervine. The yield was about 0·3 gram per kilo. The ammoniacal solution, after removal of ether, was further treated with chloroform, when pseudojervine was obtained. Protoveratridine is not obtained by this metaphosphoric acid process, which would indicate this base to be a decomposition product of protoveratrine.

Protoveratrine, $C_{32}H_{51}NO_{11}$, crystallises from dilute solutions in microscopic four-sided plates, which melt with charring at 245—250°. The base is insoluble in water, benzene, and light petroleum; chloroform and boiling 96 per cent. alcohol dissolve it somewhat; cold ether scarcely touches it, boiling ether takes up a little more. Dilute acids, with the exception of acetic acid, dissolve it. The base is exceedingly poisonous; a minute amount applied to the nose causes violent sneezing. Concentrated sulphuric acid dissolves the alkaloïd slowly with the production of a greenish colour, which passes to cornflower blue, and after some hours becomes violet. With the same acid and sugar, the first formed greenish colour becomes olive-green, then dirty green and finally dark brown; this is very different from the colours yielded by veratrine. When warmed with the strong acid, the solution is first light, then dark cherry-red, and exhales the odour of isobutyric acid. Concentrated hydrochloric and phosphoric acids give the same reaction. Dilute solutions of salts of this base are quantitatively precipitated by ammonia; precipitates are also produced by Nessler's test, gold chloride, potassium mercury iodide, potassium cadmium iodide, phosphotungstic acid, and picric acid, whilst no precipitate is produced by tannin, platinic chloride, or mercuric chloride. The aurochloride, a golden-yellow, amorphous compound, was obtained and analysed.

Protoveratridine, $C_{26}H_{45}NO_8$, occurs as colourless, four-sided plates, which melt at 265°. It is almost insoluble in alcohol, chloroform, methyl alcohol, and acetone, and insoluble in benzene, light petroleum, and ether. It is not poisonous, and does not cause sneezing, but its solution in dilute acids has a very bitter taste. Concentrated sulphuric acid gives first a violet, then a cherry-red colour. Its solution in concentrated hydrochloric acid becomes light-red on warming, as is the case with veratrine, but with a decided odour of isobutyric acid. Dilute acids readily dissolve the base, and the solutions give crystalline precipitates with ammonia. The sulphuric acid solution gives copious precipitates with phosphotungstic, picric, and tannic acids, and with potassium mercury iodide, but gives no precipitate with platinum chloride, potassium cadmium iodide, or with Millon's reagent. *Protoveratridine platinochloride*, $(C_{26}H_{45}NO_8)_2,H_2PtCl_6 + 6H_2O$, was precipitated as large, six-sided plates on adding alcohol to a mixed solution of platinum chloride and a salt of the base. Pseudojervine has been already described by Wright and Luff; they found its melting point to be 299°; the author makes it 300° to 307°. Jervine, $C_{26}H_{37}NO_3$, melts at 238° to 242°, Wright and Luff found 237°. The hydrochloride, nitrate, platinochloride, and aurochloride are described. Wright and Luff's formula is confirmed, and not the one given by Tobien. Rubijervine, $C_{26}H_{43}NO_2 + H_2O$, melts at 240° to 246°; Wright and Luff found 236°. Five basic compounds have thus been determined with certainty in white hellebore root. J. T.

Cytisine. By A. PARTHEIL (*Ber.* **23**, 3201—3203).—The alkaloïd prepared by Husemann and Marmé from the seeds of the laburnum and other kinds of *Cytisus*, to which they gave the name of cytisine, may be readily obtained in the following manner. The coarsely-powdered seeds are extracted with alcohol containing hydrochloric acid, the alcohol distilled off, the residue treated with water, and filtered through a wet filter to remove any fatty oil, the filtrate treated with lead acetate, and after separating the precipitated colouring matter, made alkaline with caustic potash, and shaken with amyl alcohol. The latter solution is then extracted with dilute hydrochloric acid, the solution evaporated, the crude cytisine hydrochloride thus obtained treated with dilute alcohol to remove colouring matters, and recrystallised several times from water. The salt then forms well-developed, colourless, transparent prisms. Its *platinochloride* crystallises in golden-yellow needles, which have the composition $C_{11}H_{14}N_2O,H_2PtCl_6 + 2\frac{1}{2}H_2O$, are tolerably soluble in water, and decompose on heating without melting. The *aurochloride*, $C_{11}H_{14}N_2O,HAuCl_4$, crystallises in short, reddish-brown, hook-shaped needles, which melt at 212—213° (uncorr.) with evolution of gas. From the analyses of these double salts, it follows that cytisine has the composition $C_{11}H_{14}N_2O$, and not $C_{20}H_{27}N_3O$ as given by Husemann and Marmé. The same formula has already been given by Gerrard to ulexine, obtained from the seeds of *Ulex europæus* (Abstr., 1886, 1048), which, as Koberth as already suggested, on physiological grounds (*Deutsch. Med. Wochenschr.*, 1890, 406) may be identical with cytisine. Both compounds are being at present further investigated.

H. G. C.

Products of the Artificial Digestion of Glue. By F. KLUG (*Chem. Centr.*, 1890, ii, 318—319; from *Centr. Physiol.*, **4**, 189—191). —Glue, obtained from the refining of fine French gelatin, is precipitated from its solution by picric acid, chromic acid, tannin, platinic chloride, mercuric chloride and iodide, potassium iodide, and hydrochloric acid. These precipitates dissolve in hot water, and are reprecipitated on cooling. Alcohol, phosphotungstic acid, and hydrochloric acid, basic lead acetate, and ammonium sulphate also precipitate it, the precipitates being, however, insoluble in hot water. With sodium hydroxide and copper sulphate, its solution is coloured violet-blue. Acetic acid and potassium ferrocyanide cause no precipitation. Millon's reagent causes a flocculent precipitate, soluble in the hot liquid; if the solution be boiled, it is coloured red. Nitric acid and sodium hydroxide colour hot glue solutions slightly yellow; copper sulphate causes a blue coloration. Glue, therefore, may be distinguished from egg albumin by the precipitate obtained with picric acid dissolving on heating and by the biuret reaction, whereas with nitric acid neither precipitation nor yellow coloration ensues. It is to be noted, however, that concentrated solutions of sodium chloride, ammonium sulphate, and gallic acid form precipitates with picric acid which dissolve in warm liquids. By artificial digestion, glue becomes converted into three substances, *glutose* and *glutinopeptone*, which dissolve, and *apoglutin*, which remains in the liquid as a flocculent residue, to the amount of 5·69 per cent.

Apoglutin dissolves completely in sulphuric acid, but only imperfectly in the other mineral acids and in acetic acid. When boiled with nitric acid, it becomes coloured yellow; sodium hydroxide and copper sulphate colour it violet; boiled with Millon's reagent, it is coloured red; it is not digested by pancreatic juice.

Glutose is precipitated from the solution of digested glue by the addition of ammonium sulphate or alcohol, and it may be precipitated, after re-solution in water, by addition of sodium chloride, and then acetic acid and concentrated solution of sodium chloride. That part which is precipitated by salt has been named by the author *protoglutose*; the remaining portion, which is separated on the addition of acetic acid and sodium chloride, he names *deuteroglutose.* Glutose, precipitated by 95 per cent. alcohol, separates as a sticky, white mass. It is also precipitated by picric and chromic acids, phosphotungstic acid and hydrochloric acid, mercuric iodide, potassium iodide and hydrochloric acid, platinic chloride, and mercuric chloride; all these precipitates, that by phosphotungstic acid excepted, are dissolved on warming the solutions, and are again precipitated on cooling. When boiled with nitric acid, it is neither precipitated nor coloured yellow; but if sodium hydroxide is added, the solution becomes yellow. Sodium hydroxide and dilute copper sulphate colour the solution violet-red; copper sulphate alone colours it blue.

Glutinopeptone is also obtained by the digestion of glutose, and may be precipitated by means of a mixture of alcohol and ether. When dried on the water-bath and in the desiccator, it appears as a yellow, brittle mass, very readily soluble in water, which distinguishes it readily from glutose. Picric acid causes a precipitate only with concentrated solutions, which redissolves in an excess of the reagent, and also by heating; chromic acid and platinic chloride cause no precipitation; sodium hydroxide and highly dilute copper sulphate solution cause a rose-red coloration; copper sulphate alone, a green coloration; Millon's reagent causes a milkiness, which redissolves on boiling. It becomes precipitated by saturating the solution with either sodium chloride or ammonium sulphate. The following are the elementary analyses of glue, apoglutin, and glutose.

	C.	H.	N.	O and S.	Ash.
Glue........	42·75	7·00	15·61	34·64	0·88
Apoglutin ...	48·39	7·50	14·02	30·09	5·22
Glutose	40·06	7·02	15·86	37·06	2·14

J. W. L.

Physiological Chemistry.

Proteïd Absorption. By R. Neumeister (*Zeit. Biol.*, **27**, 309—373).—Many observers have found that a proteïd may be absorbed without previous conversion into peptone; for instance, in the case of nutrient enemata. It also appears that a first stage in the action of the digestive juices is simply to dissolve the proteïd; changes of the nature of hydration then follow. Hasebroek (Abstr., 1887, 609) showed that this was the case with fibrin. It is equally true for coagulated white of egg, although whether the dissolved albumin is the same as the original albumin is uncertain; it is certainly not a globulin; serum albumin, vitellin, and other proteïds are also similarly simply dissolved, in the first instance, by the gastric and pancreatic secretions. Caseïn and hæmoglobin are exceptions to this rule. Caseïn is first converted into an insoluble curd by the rennin of the stomach, and hæmoglobin is decomposed into hæmatin and a proteïd residue.

When various proteïds are introduced directly into the blood stream, there are differences again noticeable. Caseïn and hæmoglobin solutions act like foreign substances, and are excreted by the kidneys. Egg albumin is similarly got rid of; but in case of blood transfusion, there is no albuminuria; the same is true for the injection of serum, or of solutions of pure serum albumin, of syntonin (prepared either from white of egg or myosin), and of crystalline phytovitellin. These proteïds, among which are to be noted several which are not normal constituents of the blood, are thus directly assimilable, without having undergone peptonisation.

In fact, it is well known that albumoses and peptones introduced into the circulation are not assimilable, but, like other foreign substances, are excreted by the kidneys (compare Abstr., 1888, 516). Dextrose is similarly got rid of, if its percentage in the blood is higher than normal; the question thus arises, whether peptone should be considered as on all fours with dextrose in this respect. That it cannot be, but that it is an absolutely foreign substance is shown by the fact that practically it all appears in the urine, and that in normal blood no peptone or peptone-like substance is present. The word peptone may here be conveniently employed to include the albumoses, for all these products of proteolysis are in this respect the same (including hetero-albumose and atmidalbumin, concerning which experiments are now, for the first time, given).

Peptone thus disappears rapidly from the blood after injection; this occurs also when none can escape from the kidneys, either by ligaturing the ureters, or by injecting such a large amount that the lowering of blood pressure so produced stops urinary secretion. Under these circumstances, it is discharged into the intestinal canal.

Peptone is therefore a form of proteïd not assimilable by living cells. Previous experimenters have attempted to answer the question where the peptone formed in the alimentary canal is reconverted into normal proteïds. Salvioli could find none in the blood circulating in the stomach walls, although the stomach was full of peptone. Hofmeister corroborated this; and in the present research a number of observations, in which an artificial circulation was kept up, led to the same conclusion that some element, either in the interior of the alimentary canal or in the wall of the same, effects the disappearance of peptone; no other tissue produces this change. The general outcome of these experiments is as follows; without doubting the existence of micro-organisms which cause the disappearance of peptone (*M. restituens* of J. Brinck, Abstr., 1889, 632; compare also N. Popoff, Abstr., 1889, 632), it is probable that the regeneration of albumin from peptone occurs not before, but concomitantly with, absorption. The methods of Brinck and Popoff were not carefully conducted from a chemical standpoint; no doubt their peptone was mixed with albumin; they put this mixture into the stomach, and withdrew it after half-an-hour; by that time the peptone had been absorbed, and the fluid, *minus* its peptone, was now able to keep the frog's heart beating; whereas, their conclusion was that the peptone had been converted into serum albumin. The question then arises, do the lymphoïd cells or the epithelium cells of the stomach and intestinal walls produce this effect? The fact that the white blood corpuscles are not able to effect the change when peptone is injected into the blood stream is considered sufficient to refute the conclusion arrived at by others that the lymph cells are the active agents; in fact, most physiologists are now pretty well agreed that it is the epithelial elements with which, in this connection, we have to reckon, and their dehydrating action on the peptones is comparable to that of the liver cells in converting sugar into glycogen.

The question whether the liver cells have any action on peptone is an interesting one. In most animals, artificial circulation of fluid containing peptone through the recently-removed and still-living organ led to a negative result; but in the case of the rabbit, the liver cells were found to possess the power seemingly limited in other animals to the columnar cells of the wall of the alimentary canal. It cannot be, however, supposed that weighty conclusions can be drawn from an exceptional case; and even in the rabbit, the liver cells cannot normally fulfil this function, since the portal vein is always free from peptone, as in other animals. Such observations are also of importance in view of Seegen's remarkable conclusion that the formation of sugar in the liver occurs, not at the expense of the hepatic glycogen, but of the peptone brought to the liver by the portal vein (Abstr., 1888, 172). Much of the present paper is devoted to an examination of Seegen's work, and the general nature of the criticisms, and of the experiments performed to negative his assertions, will be gathered from what has preceded this.

Throughout this paper, great care is taken to point out the methods to be adopted in the separation of peptones and albumoses from one another, and from other proteïds, and the fallacious results obtained before the time of the introduction of ammonium sulphate as a reagent for this purpose. Among the points taken up, it is shown that a so-called peptone described as existing in eggs (W. Fischel, Abstr., 1886, 166) is not a true peptone. The name *pseudopeptone* is suggested for it. W. D. H.

Cystin in Pancreatic Digestion. By E. Külz (*Zeit. Biol.*, **27**, 415—417).—The question, as to what becomes of the sulphur of proteïds during digestion has never been completely answered. In the present examination of the products of an artificial pancreatic digestion, no hydrogen sulphide was evolved. The insoluble products were removed by filtration, and the filtrate concentrated; during this process, a precipitate formed, but after removal this was not found to contain cystin. The final filtrate, after a time, deposited a white precipitate insoluble in water, but soluble in ammonia. The ammoniacal solution was diluted with large quantities of water, and six-sided crystals separated, which, after purification by recrystallisation, gave all the reactions of cystin. Whether this is always the case, or if bacteria are concerned in the process, are questions that have still to be settled. W. D. H.

The so-called Liver of Helix pomatia. By M. Levy (*Zeit. Biol.*, **27**, 398—414).—The chief intestinal gland of the snail *Helix pomatia* is a digestive gland, but is not analogous to any of the abdominal glands of the higher animals. The weight of its organic constituents is very constant, being the same in summer and winter, and in great measure they are the same in kind in all periods of the year. The alcoholic extract of the gland shows the chlorophyll spectrum (MacMunn's enterochlorophyll). The digestive ferments present are a diastatic, a peptic, but not a tryptic one. The peptic ferment appears to be identical with Krukenberg's helicopepsin. The diastatic ferment disappears during the winter sleep; it is capable of digesting raw starch, but has no effect on cellulose. A fat emulsifying action is shown by the secretion in the summer time, but this also disappears during hibernation.

The ferment by means of which this action is brought about is not identical with the one described by Schmiedeberg (*Arch. exper. Path. Pharm.*, **14**) as histozyme. Histozyme, which was separated from pigs' kidneys, is concerned in the splitting up of hippuric acid. The snail's ferment has no such action.

Glycogen with sinistrin was generally present in the organ, but all tests for bile gave a negative result. Jecorin was also absent.

A list of the substances separable from the organ is as follows:—

(1.) In the alcoholic extract: Chlorophyll, lecithin, oleïc acid, fatty acids, ash, chlorine, and phosphoric and sulphuric acids.

(2.) In the ethereal extract: A trace of fat.

(3.) In the aqueous extract: Sugar, globulin (coagulating at 66°), glycogen, sinistrin, hypoxanthine, and other bases precipitable by phosphotungstic acid; in the ash, potassium, sodium, calcium, magnesium, iron (traces), manganese, chlorine, and phosphoric and sulphuric acids. In winter animals, silica was found in addition.

W. D. H.

Organic Basis of Various Shells. By W. ENGEL (*Zeit. Biol.*, **27**, 374—385).—Numerous previous researches have been directed to the determination of the inorganic constituents of egg shells, but those relating to their organic constituents are scanty.

The shells of a number of snakes, which were preserved for microscopic purposes in Kleinenberg's solution, were freed from picric acid by prolonged washing with water, alcohol, and ammonia. Elementary analysis of their organic substratum gave the following percentage results:—C, 54·68; N, 16·37; H, 7·24; O, 21·1. These coincide very well with the percentage composition of elastin, as worked out by previous investigators. The reactions of this substance are, moreover, identical with those of elastin; some slight differences in solubility, especially in alkalis, are not considered sufficient to negative the general conclusion that the material in question is elastin, since elastin prepared from various sources itself exhibits similar differences in solubility.

The cover of the incubating cells of wasps was next investigated; and although the quantity of material available was not sufficient for elementary analysis, the colour tests and solubilities of the substance are so like those of fibroïn, with which it was carefully compared, that the conclusion is drawn that the material in question is fibroïn.

Lastly the egg shells of the Aplysia were examined; their organic constituent appeared to be allied to keratin by its reactions, and in-elementary analysis it was found to be intermediate between conchiolin and elastin. The general conclusion drawn is that the substance in question is one of the keratins. W. D. H.

Action of Yeast on the Animal and Human Organism. By J. Neumayer (*Chem. Centr.*, 1890, ii, 247—248; from *Inaug. Diss. München. Hygien. Inst.*).—The author finds that the various yeasts pass through the alimentary canal without suffering any change, and are not acted on by the gastric juice, and that they may be eaten without any harm to the animal, provided that all fermentable substances are absent, otherwise inflammation of the stomach ensues. This injurious action is not due to the yeasts, or the principal products of their fermentive action, but to abnormal fermentation products formed at the high temperature of the body; if the fermentation proceeds at low temperatures, these injurious products are not formed at all, or only in insignificant amount. Subcutaneous injection of the yeasts causes their destruction, without, however, producing any ill effects on the animal. J. W. L.

Chemistry of Vegetable Physiology and Agriculture.

The Antiseptic Properties of Sodium Fluoride. By O. Hewelke (*Chem. Centr.*, 1890, ii, 248; from *Deut. Med. Wiss.*, **16**, 477—478).—The author experimented with alkaline sodium fluoride on the ferment, and the alkaline fermentation of urine. *Torula cerevisœ* did not grow in the presence of 1 part of sodium fluoride in 100 to 300 parts of urine; in presence of 1 : 600 to 3000 the fermentation was distinctly checked, and this was noticeable, although in a minor degree, when the proportion of sodium fluoride was reduced to 1 : 4000. In the case of urine without any sodium fluoride, the fermentation commenced at the end of 3 to 5 days; the addition of 1 part to 2000 of urine prevented fermentation until the 14th—15th day; 1 : 600 till the 60th day; 1 : 100 over a month. Blood, with the addition of 1 part of sodium fluoride to 80—160, remained good for a long period, and a disagreeable odour was first developed at the end of several weeks.

In nutrient substances containing 1 of sodium fluoride : 150 to 200, neither pathogenic nor non-pathogenic organisms developed, and even when the proportion of the salt was reduced to 1 : 600, evidences of a checked growth were observable. Some organisms proved more susceptible than others, for instance 1 : 300 prevented the growth of *Bacillus anthracis*. In general, the pathogenic organisms proved the most susceptible. J. W. L.

Catalytic Reduction of the Sulphonic Group. By O. Loew (*Ber.*, **23**, 3125—3126).—As, in all probability, the sulphur in albuminoïds is not present in the form of a sulphonic group, it must be assumed that hydrogen sulphide is formed from sulphates in the vegetable organism, and that at the moment of its formation it is further converted into an organic compound, that is to say, it takes part in the production of albuminoïds.

The most plausible explanation of this phenomenon is, that the intense atomic vibrations in the active albumin are communicated to the sulphates and to the dissolved organic matter, causing them to act on one another in such a way that the oxygen of the sulphuric acid acts on the organic matter, the hydrogen of the latter combining with the sulphur; in other words, it may be supposed that oxidation and reduction take place simultaneously under the influence of a catalytic action.

Experiments which were made with various sulphates in presence of platinum black did not give the expected results; sodium hydroxymethylenesulphonate (formaldehyde sodium hydrogen sulphite), on the other hand, is reduced moderately easily. On warming a solution of this organic salt (5 grams) and crystalline sodium carbonate (10 grams) in water (100 grams) with platinum black (16 grams), in a flask which is almost completely filled with the solution, an odour of leeks is observed after some hours, and the solution then gives the nitroprusside reaction for sulphides; on acidifying with acetic acid, hydrogen sulphide is evolved, showing that sodium sulphide has been formed by reduction, whilst a corresponding quantity of the sodium hydroxmethylenesulphonate must have undergone oxidation. When the quantity of the organic sodium salt and platinum black is increased, the solution gives off an odour very like that of decomposing albuminoïds, probably owing to the formation of methyl mercaptan; if platinum black is not added to the solution, reduction does not take place. The above reaction is not due to nascent hydrogen, as this gas is not evolved when a dilute solution of formaldehyde is warmed with platinum black and sodium carbonate.
F. S. K.

Chemical Composition of Vegetable Cell Membranes. By E. Schulze (*Ber.*, **23**, 3175; compare Abstr., 1890, 1456).—The author explains that he did not mean it to be inferred that cellulose is the only constituent of the cell envelope which is insoluble in dilute acids.
J. B. T.

Crystalline Constituents of the Seeds of Cataputiæ minoris. By Y. Tahara (*Ber.*, **23**, 3347—3351).—The seeds are carefully freed from oil, extracted repeatedly with alcohol, the alcohol evaporated, the residue washed with ether, and boiled with alcohol; on cooling the solution, brown crystals of ausculetol are deposited, which may be purified by treatment with lead acetate.

If the oil is allowed to remain for some time in a closed flask, a substance separates which crystallises from alcohol in colourless, odourless prisms melting at 193°; it is insoluble in water, alkalis, or acids, and has not yet been further investigated.
J. B. T.

Kesso Oil. By J. Bertram and E. Gildemeister (*Arch. Pharm.*, **228**, 483—492).—Kesso is the Japanese name for *Valeriana officinalis* *var. angustifolia;* the oil obtained by distilling the root of this plant with steam has a sp. gr. of 0·996, whilst the sp. gr. of oil of valerian is 0·945.

A large quantity of kesso oil was divided into three portions by distillation with steam. The first portion was fractionated into six portions. 1. Up to 155°, contained much acetic and valeric acids, but no formic acid. Probably some valeraldehyde was present, judging by the odour. 2. That boiling between 155° and 160° was relatively small in amount, and consisted of lævopinene, the rotation in Wild's apparatus, with a column 100 mm. long, being 53° 5′ to the left. 3. That boiling between 160° and 170° is not given. 4. That boiling between 170° and 180° consisted of dipentene, as shown by the formation of its hydrochloride and hydrobromide. 5. That boiling between 180° and 200° is not given. 6. That boiling between 200° and 220° contained terpinol, $C_{10}H_{17}\cdot OH$. On shaking it up with a strong aqueous hydriodic acid solution, the compound $C_{10}H_{16},2HI$ was obtained, which melted at 76°. This fraction also contained borneol.

The second portion, boiling between 220° and 290°, yielded a fraction below 260°, composed of borneol with acetic and isovaleric acids. The fraction boiling between 260° and 280° was a clear liquid, consisting, apparently, of sesquiterpene.

The third portion of the distillate was heavier than water, and boiled about 300°. This was saponified, and yielded acetic acid, a bluish oil, whose composition has not yet been made out, and *kessyl alcohol*, $C_{14}H_{24}O_2$. This alcohol is odourless, insoluble in water, easily soluble in alcohol, ether, chloroform, benzene, and light petroleum. It melts at 85°, and boils under a pressure of 11 mm. between 155° and 156°, and at the ordinary pressure at 300—302° without decomposition. A 10 per cent. solution in alcohol has a rotatory power of 3° 39′ to the left in a column 100 mm. long. It readily forms well-shaped, rhombic crystals from its solution in alcohol or ether [$a : b : c = 0{\cdot}9936 : 1 : 0{\cdot}4369$]. Kessyl alcohol alone, or dissolved in dry ether, in contact with acetic chloride or phosphorus pentachloride, develops heat, evolves hydrogen chloride, and produces a splendid, dark, cherry-red solution. *Kessyl acetate*, $C_{14}H_{23}O_2Ac$, was obtained by heating the alcohol with acetic anhydride and some anhydrous sodium acetate. It can also be obtained by fractional distillation of the kesso oil, but is impure when thus produced. The pure acetate is a thick, colourless oil, of very faint odour, which does not solidify at −20°. It is insoluble in water, easily soluble in ether, alcohol, chloroform, and light petroleum. Its is lævorotatory to the extent of 70° 6′ in a column 100 mm. long. Oxidation products of kessyl alcohol have not yet been fully investigated. J. T.

Poisonous Action of Hydrazine. By O. Loew (*Ber.*, **23**, 3203—3206).—Hydrazine exerts an extremely poisonous action on organisms of the most varying description. In a solution containing, in addition to food substances, 0·2 gram of hydrazine sulphate per litre, the shoots of the helianthus and of barley were rapidly killed. Algæ, fission organisms, moulds, *Schizomycetes*, and lower water organisms were also rapidly destroyed by its dilute solution. A dose of 0·1 gram of hydrazine sulphate neutralised with sodium carbonate, and administered subcutaneously to a guinea-pig, caused death in 2¼ hours, and a dose of 0·5 gram, administered to a puppy in a similar manner, brought about the same result in 2½ hours. H. G. C.

Composition of Sorghum Seed. By H. W. Wiley (*Bied. Centr.*, 1890, 678—680).—The following is the mean percentage composition of 24 samples sorghum seed, hulled and unhulled:—

	Unhulled.	Hulled.
Moisture	9·93	9·63
Albuminoïds	10·54	11·39
Light petroleum extractive	3·72	3·16
Ether extractive	0·61	0·54
Absolute alcohol extractive	2·44	1·46
80 per cent. alcohol extractive	2·91	1·78
Fibre	3·17	1·83
Ash	2·05	1·69
Carbohydrates	64·62	68·86

This seed, compared with wheat, maize, and oats, appears to be equal in feeding value to maize and oats, and only rather poorer than wheat.

The seed hulls contain a colouring matter which, however, is not harmful to cattle, nor does it contain any tannin. E. W. P.

Analytical Chemistry.

Gas Apparatus, &c. By W. E. Adeney (*Chem. News*, **62**, 196—199; 204—206).—In this apparatus, the pressure and measuring tubes are placed some little distance apart, the latter only being surrounded by a water-jacket; they are connected at their lower extremities (which are bent at right angles for the purpose, the measuring tube being likewise narrowed) by wired india-rubber tubing and a glycerol joint. The pressure tube is furnished near the bend with a side tube connecting with the mercury reservoir, and terminates at the top with a Friedrich's patent glass stop-cock, so that it can be used either open or closed; it is 1000 mm. high. The measuring tube, 640 mm. long, is wide for about two-thirds of its length, but is narrower at the upper portion, to which a Friedrich stop-cock is attached, and this is connected with two capillary, double right-angled tubes, one of wider bore, for the admission of the gas to be examined, or other object; the second and narrower one passing to the laboratory vessel, which is furnished at the top with a cup, into which the tube fits, and is rendered air-tight by an india-rubber collar. The laboratory vessel, which may be of any convenient capacity, is provided with platinum wires for explosions, and, moreover, terminates below in a narrow cylindrical portion, which may be used open, or be closed with a cork, and to which is attached a side tube, connecting with an independent mercury reservoir to facilitate filling with mercury, transferences, &c. A suitably bent tube, with india-rubber attachment, is fitted to the cork, and serves for the admission of reagents. Behind the whole length of the pressure tube a long, narrow mirror, graduated in millimetres on an unsilvered portion, is fixed at such an angle as to reflect a good image of the mercury column and meniscus. The whole apparatus is mounted on a wooden support, with necessary clamps, attachments, &c.; the mercury reservoirs being placed behind. The apparatus serves for all kinds of gas measurements, as an air-pump, and for distillations under reduced pressure or in a vacuum. D. A. L.

Lacmoïd. By O. Förster (*Zeit. ang. Chem.*, 1890, 163—167).—Commercial lacmoïd is of very variable character. Some specimens are almost wholly insoluble in water, and are unsuitable as indicators. Others colour boiling water intensely blue, and are fit for use. To prepare the pure blue indicator, the finely-powdered crude material is extracted with boiling water, but stopping short of complete exhaustion, so as to avoid dissolving a sparingly soluble red substance. From the cooled and filtered blue solution, the colour is precipitated by feebly acidifying, and after some hours is collected on a filter and washed with cold water, then dried at a low temperature (since some decomposition takes place if it be dried at 100°), or dissolved in alcohol, and the solution evaporated on the water-bath. Purified in this way, it gives, with pure distilled water, a blue solution, having a slight tendency to violet, and exceeds all other indicators in sharpness. In water containing carbonic acid or an ammonium salt, it gives an exceedingly sharp change with a quantity of alkali, which has scarcely any effect on litmus. To prepare blue lacmoïd paper, sulphuric acid is added to an alcoholic solution of lacmoïd, until white paper dipped into the liquid is coloured red. This will become blue on drying. The depth of blue should be that of the forget-me-not. For red paper, the paper should be dipped in very dilute sulphuric acid and dried before staining. It must be preserved in well stoppered bottles, and is an extremely sensitive indicator for alkalis.

A somewhat more ready mode of purification is as follows:—8 parts of finely-powdered crude lacmoïd is gently warmed for a quarter of an hour with 100 parts of 20 per cent. alcohol, and the liquid filtered after cooling. After ascertaining the amount of matter in solution by evaporating a portion, there should be added an alcoholic solution of 14 parts of malachite green to 86 parts of the lacmoïd. This addition does not impair the indication with acids, whilst it increases enormously the sharpness of the change to blue with an alkali. The liquid is filtered from a precipitate which forms, and is then mixed with an equal volume of absolute alcohol. It should be kept in black bottles. M. J. S.

Estimation of Free Hydrochloric Acid in Stannous Chloride Solutions. By W. Minor (*Zeit. ang. Chem.*, 1890, 25—26).—Precipitation as silver chloride cannot be resorted to in consequence of the co-precipitation of tin compounds. A measured quantity (100 c.c.) of the solution is, therefore, saturated hot with hydrogen sulphide, and filtered into a litre flask. Half of the filtrate is boiled to expel hydrogen sulphide, and the total acid then titrated with standard alkali. The amount of tin is now ascertained by titration with iodine, and the corresponding quantity of hydrochloric acid deducted from the total. M. J. S.

Detection of Hypochlorous Acid in Chlorine Water. By T. SALZER (*Chem. Centr.*, 1890, ii, 472; from *Pharm. Zeit.*, **35**, 457).—The author recommends the method of Lunge and Naeff, devised for the determination of hypochlorous acid in the presence of chlorine, which depends on the fact that chlorine reacts with potassium iodide and hydrochloric acid, forming potassium chloride, iodine, and hydrochloric acid, whereas hypochlorous acid produces, under the same circumstances, no hydrochloric acid. If, therefore, the solution is first titrated with decinormal alkali and then with thiosulphate solution, the amount of the chlorine and hypochlorous acid may be calculated. Of neutral chlorine water, the author recommends 25 c.c. should be acidified with 10 c.c. of decinormal hydrochloric acid, 1 gram of potassium iodide added, and titrated with thiosulphate. Pure chlorine water should require exactly 10 c.c. of decinormal hydrochloric acid. Chlorine water, containing acid, is not to be recommended as an eye-wash. J. W. L.

Detection of Traces of Iodine in the Presence of much Chlorine. By A. JOHNSTONE (*Chem. News*, **62**, 153, 169).—The solution to be tested is treated with a saturated solution of silver nitrate in strong ammonia; a yellow precipitate indicates the presence of an iodide. To confirm this, add concentrated sulphuric acid, and agitate with carbon bisulphide; the latter becomes coloured by any liberated iodine. D. A. L.

Separation and Estimation of Tellurium. By E. DONATH (*Zeit. ang. Chem.*, 1890, 214—217).—Precipitation by sulphurous acid is complete but tedious. Kastner's grape-sugar method (Abstr., 1876, 440) is accurate and expeditious. Precipitation by stannous chloride or an alkaline stannite is not suitable, since the precipitate always contains tin. Tellurium is very rapidly precipitated from acid solutions by hyposulphurous acid. The yellow solution obtained by shaking scrap zinc with aqueous sulphurous acid is filtered, and added to the cold concentrated hydrochloric acid solution of the tellurium compound. Precipitation is complete in 15 minutes. The washed precipitate, which may contain some tellurium sulphide, is rinsed into a tared capsule, oxidised with strong nitric acid, and, after gentle ignition, weighed as tellurium dioxide.

For the attack of ores containing tellurium, 3 or 4 grams of the impalpable powder is treated in a basin with small quantities of concentrated nitric acid, and from the pasty mass obtained, the excess of acid is completely evaporated at a temperature which will not decompose the metallic nitrates. The dry mass is powdered in the basin, moistened with strong soda solution, and digested for half an hour. Water is then added, the filtrate boiled for 20 minutes with pure grape-sugar, and the precipitated tellurium weighed as dioxide, as above.

M. J. S.

Estimation of Hypophosphorous, Phosphorous, and Hypophosphoric Acids. By L. Amat (*Compt. rend.*, **111**, 676—679).—In a warm acid solution, hypophosphoric acid reduces mercuric chloride to the mercurous salt, and is itself completely converted into phosphoric acid, probably in consequence of an intermediate conversion into phosphorous and phosphoric acids. About 1 gram of the substance is mixed with 10 c.c. of concentrated hydrochloric acid, evaporated almost to dryness in order to promote the decomposition of the hypophosphoric acid, redissolved in a small quantity of water, and mixed with a solution containing 68 grams of mercuric chloride and 20 to 40 c.c. of concentrated hydrochloric acid per litre. The mixture is allowed to remain for 24 hours at 80°, and the mercurous chloride is collected and weighed.

Potassium permanganate can be employed in the manner indicated by P. de St. Gilles, the substance being oxidised by excess of the permanganate and the excess determined by means of oxalic acid. The oxidation is more rapid, the more concentrated the solution, the greater the proportion of free acid, and the higher the temperature. At a high temperature, a small quantity of permanganate may be decomposed, and at a low temperature, especially in dilute solutions, oxidation is incomplete; careful attention to the conditions is therefore necessary.

The permanganate employed should be equivalent to a solution containing 63 grams of oxalic acid per litre, and the quantity of substance taken for analysis should reduce about 20 c.c. of the permanganate. The substance is dissolved in 20 c.c. of water, mixed with 3 c.c. of concentrated sulphuric acid, cooled, mixed with 35 c.c. of permanganate, and heated at 50° for half an hour. 20 c.c. of oxalic acid solution is then added, and after the liquid has become colourless and the brown precipitate has completely dissolved, the excess of oxalic acid is determined by means of permanganate. The method is applicable to phosphites, pyrophosphites, and hypophosphites. In the case of hypophosphates, the liquid is first heated with the sulphuric acid at 80—100° for half an hour, and then cooled and mixed with the permanganate.

The mercuric chloride method, although the more tedious, is the more accurate of the two.

C. H. B.

The "Citrate Method" of Phosphoric Acid Estimation. By O. Reitmair (*Zeit. ang. Chem.*, 1890, 19—25, 196—210; continued from Abstr., 1890, 416).—Comparing the results yielded by the citrate method, under a great variety of conditions, with those furnished by precipitation by molybdate, the author has investigated the amount of the error of deficiency due to imperfect precipitation of the phosphoric acid, and that of the error of excess due to contamination of the precipitate by impurities. His conclusions are as follows:—In all modifications of the citrate method, the precipitation of the phosphoric acid is incomplete, and with large proportions of citrate and a small amount of magnesia, it may be very seriously so. In the most favourable cases, about 2 milligrams of magnesium pyrophosphate passes into the filtrate. On the other hand, when calcium, iron, aluminium, or manganese is present, a variable portion of those bases will always be found in the precipitate, and, if enough magnesia mixture has been used, a compensation of errors is possible. The use of a minimum quantity of ammonium citrate, in accordance with the procedure of Brassier and Glaser (Abstr., 1885, 837), is not permissible; an excess is always requisite. The quantity of magnesia mixture must, however, always be proportioned to the amount of citrate. The bases which chiefly contaminate the precipitate are calcium and manganese. Both are precipitated in the form of ammonio-phosphates, which are converted into pyrophosphates on ignition. Of iron and aluminium, there are usually only traces precipitated; the principal effect of these metals in the solution is to retard the precipitation of the magnesium ammonium phosphate. Grupe and Tollens have stated that magnesia, or a basic magnesium salt, is precipitated together with the ammoniophosphate. This is certainly true, since the ignited precipitate always shows the reaction of an orthophosphate with silver nitrate, but if the magnesia mixture has been added by drops to an ammoniacal solution (2·5 per cent. of ammonia), the magnesium oxide in the precipitate will be scarcely weighable. But, using nearly neutral solutions, and especially when salts of sodium or potassium are present, the amount may be very considerable. The use of hydrochloric acid for dissolving phosphates containing silica is disadvantageous; the magnesium precipitate will always be strongly contaminated with silica, and the amount of foreign bases precipitated will also be increased. Even when sulphuric acid is used, and the solution is consequently freer from silica, it is to be expected that about 1 milligram will be found in the precipitate. The presence of sulphates has, however, the tendency, other things being equal, to increase the error of deficiency. Moreover, since the use of sulphuric acid removes a large part of the lime as sulphate, less ammonium citrate is needed than would otherwise be the case.

Using the process for estimating the phosphoric acid in the soluble portion of a superphosphate, and working upon 1 gram of substance, with 5 grams of citric acid, 25 c.c. of magnesia mixture, and ammonia equal to 2·5 per cent. of the solution, a loss of about 2 milligrams, equal to 0·128 per cent. of phosphoric acid, may be assumed. On the other hand, when examining basic slag, or raw phosphates, the error will be in excess. If silica and manganese are absent, the amount of the error may be small, but no estimate of its average magnitude can be formed. M. J. S.

Reduction of Arsenic Acid in Analysis. By F. A. GOOCH and P. E. BROWNING (*Amer. J. Sci.*, **40**, 66—71).—The authors endeavour to shorten the process of reduction of arsenic acid by employing hydriodic acid, instead of sulphurous acid, as the active agent. The process recommended may be summarised as follows:—To the arsenate in solution are to be added potassium iodide in excess of the amount needed, according to the equation, to complete the reduction, and 10 c.c. of half and half sulphuric acid. The liquid is to be diluted to about 100 c.c., and boiled rapidly until the volume is decreased to 40 c.c. The colour of the free iodine is to be bleached by cautious additions of sulphurous acid, and the liquid immediately diluted with water and neutralised, first with normal potassium carbonate and afterwards with the hydrogen salt. The whole is to be cooled and titrated with iodine in the usual manner, starch being used as an indicator. The advantage of this method is in the rapidity with which it may be executed, the whole operation being completed in half an hour. The average error of the process amounts to 0·13 per cent. of the amount taken. B. H. B.

Estimation of Peroxides of the Alkaline Earths. By G. Kassner (*Arch. Pharm.*, **228**, 432—435).—A weighed amount of the peroxide (0·2 in the case of the barium compound) is ground with a little water and washed into a beaker; then excess (about five times as much) of pure potassium ferricyanide is added. Oxygen is at once evolved, and the reaction is complete when the gas ceases to come off; the reaction may be accelerated by gently warming the beaker. A considerable amount of water is now added, and excess of sulphuric acid; the greenish colour which may now appear does not affect the result. The solution is finally titrated with potassium permanganate solution. Thus, 0·2 gram of peroxide required 17·2 c.c. of permanganate (1 c.c. = 0·00576 gram of Fe); hence the peroxide contained 74·7 per cent. of peroxide. The old direct process gave 75·13 per cent. The new process may prove useful in cases where an acid solution would be inadmissible; it is only necessary to filter off an aliquot part of the solution before the acid is added, and then titrate and calculate.

J. T.

Estimation of Ferric Oxide and Alumina in Phosphatic Manures. By A. Stutzer (*Zeit. ang. Chem.*, 1890, 43—44).—The author, whilst admitting the superiority of Glaser's method (Abstr., 1890, 420) over that depending on the insolubility of the iron and aluminium phosphates in acetic acid, prefers to weigh the ferric oxide and alumina as such, and not as phosphates. To this end, the solution of 1 gram of the phosphate in hydrochloric acid is made alkaline with ammonia, and then feebly acid with acetic acid. The precipitate is collected and partially washed; the filter with its contents is returned to the same beaker, and digested with 150 c.c. of molybdate solution. The solution filtered from the yellow precipitate is made feebly alkaline with ammonia, and warmed for 10 minutes on the water-bath. The precipitate sometimes contains traces of molybdic acid, but if dissolved in hydrochloric acid and reprecipitated by ammonia, the ferric oxide and alumina are obtained free from all impurities.

M. J. S.

Valuation of Pyrolusite by means of Hydrogen Dioxide. By A. Baumann (*Zeit. ang. Chem.*, 1890, 72—79).—The reaction $MnO_2 + H_2O_2 = MnO + O_2$, which occurs in acid solutions, yields equally good results by gravimetric, volumetric, or gasometric methods. The last has already been employed by Lunge (Abstr., 1885, 1162). For accurate work, an ordinary 50 c.c. nitrometer is scarcely large enough, since not more than 0·18 gram of manganese dioxide could be used, and an error of 0·1 c.c. in reading the volume of the gas would equal 0·2 per cent. in the result. The eudiometer should be able to measure at least 100 c.c. of gas, and should be surrounded by a water-jacket, that the temperature may be known with exactness. Water may be used in the eudiometer instead of mercury. In case the pyrolusite should resist attack, the reaction flask may be warmed to 70°. 1 c.c. of oxygen at 0° and 760 mm. is equal to 0·003885 gram of MnO_2.

Gravimetrically, the estimation may be made by weighing the oxygen evolved. Almost any of the forms of carbonic acid apparatus for the estimation by loss of weight may be used. From 2 to 6 grams of the pyrolusite, in impalpable powder, is placed in the reaction flask with 30 c.c. of sulphuric acid (1 part to 3 of water), and 40 c.c. of commercial hydrogen peroxide is placed in the inner tube. Warming should be avoided.

For volumetric estimation, an acidified hydrogen peroxide (containing about one-tenth of sulphuric acid) should be made of strength corresponding approximately with a standard permanganate (10 grams per litre). The relation of the solutions is accurately found, and then 0·4 to 1 gram of the pyrolusite is treated with 50 c.c. of the hydrogen peroxide in the cold, and after half an hour with occasional shaking, the excess is titrated back with the permanganate. The presence of ferrous compounds in the pyrolusite leads to high results, since they consume hydrogen peroxide; in Bunsen's and the ferrous sulphate processes, the error is in the opposite direction. M. J. S.

Titration of Permanganate and of Bleaching Powder by Hydrogen Peroxide. By L. VANINO (*Zeit. ang. Chem.*, 1890, 80—83). —To facilitate calculation of the results from the volume of oxygen evolved, tables are given of the weight of 1 c.c. of oxygen and of chlorine respectively, over a sufficiently wide range of temperature and pressure. The author's practice differs in three points from that of Lunge (*Zeit. ang. Chem.*, 1890, 7); he prefers an azotometer to the nitrometer; in the analysis of bleaching powder, he uses feebly acid, instead of alkaline, hydrogen peroxide; and he compares his results with those of the iodometric method, rather than with Penot's, and finds a closer agreement than did Lunge with the latter. The titration by permanganate of the residual hydrogen peroxide gives unexceptionable results in the assay of bleaching powder. M. J. S.

Dry Assay of Tin Ores. By H. O. HOFFMANN (*Chem. News*, **62**, 157—159; 169—170).—This section of the author's paper on the dry assay of tin ores deals with methods depending on fusion with potassium cyanide, of which various modifications have been investigated, with and without a salt cover, in chalk- or charcoal-lined crucibles, in porcelain crucibles, with charcoal intermixed with the cyanide, with various qualities of cyanide, &c. The chief source of error appears to be due to the tin, instead of forming a button, being disseminated through the mass of slag, when it cannot subsequently be thoroughly separated. To obviate this, it is recommended to ram a lot of potassium cyanide into the bottom of the crucible before putting in the ore and flux, so as to form a fused mass for the tin to fall through and accumulate beneath to form a button. As regards impurities, iron passes into the cyanide, alkaline sulphates and carbonates cause low results owing to the formation of tin sulphides in the first case, and of stannates in the second. Impure cyanide gives low and irregular results.

D. A. L.

Estimation of Vanadic Acid in Vanadiotungstates. By A. Rosenheim (*Ber.*, **23**, 3208—3210).—The statement attributed to the author by Rothenbach (*Ber.*, **23**, 3050; and this vol., p. 18) that sulphurous acid is capable of reducing tungstic acid when present as phosphotungstic acid is incorrect, as he has shown (Abstr., 1889, 762) that no reducing action takes place. Rothenbach further states that the violet coloration produced when sulphurous acid is added to a mixture of phosphoric and vanadotungstic acids is not due to the reduction of the tungstic acid, as vanadium tetroxide free from sulphurous acid also yields the coloration with phosphotungstates. This fact, however, really proves the contrary of Rothenbach's statement, for vanadium tetroxide, as shown by its action on ferric oxide and ammoniacal silver solutions is a reducing agent, and this is the compound which actually causes the reduction of the tungstic acid, as is shown by the fact that the intensity of the coloration is dependent on the quantity of tungstic acid present, and not on that of the vanadium tetroxide.

H. G. C.

Estimation of Ferrocyanides. By R. Zaloziecki (*Zeit. ang. Chem.*, 1890, 210—214).—When a solution of an alkaline ferrocyanide is treated with zinc carbonate and a stream of carbonic anhydride, the whole of the ferrocyanogen is precipitated in the form of a double salt of the alkali metal and zinc. If the operation is performed at the boiling temperature, the reaction takes place according to the equation $3M'_4FeCy_6 + 2ZnCO_3 = 2Zn_2FeCy_6,M'_4FeCy_6 + 4M'_2CO_3$, and the amount of alkaline carbonate produced may be employed as a measure of the ferrocyanide originally present. The zinc carbonate should be prepared by the addition of sodium carbonate to a hot solution of zinc sulphate, as it then subsides and washes readily. It is preserved in the pasty state, and if the quantity added contains an amount of zinc approximately equal to the weight of alkaline ferrocyanide, it will be amply in excess. The mixture is heated to boiling, and a stream of carbonic anhydride is passed through it for a half to one hour. It is then cooled, diluted to a known volume, filtered, and an aliquot part of the filtrate is titrated with standard acid, using methyl-orange as indicator. If the original solution had contained alkaline carbonates or sulphides, the amount of these should be ascertained by titration, and the acid they consume deducted from the total quantity required after treatment with zinc carbonate. Sulphates and chlorides have a disturbing influence, but this can be counteracted by the presence of an excess of alkaline carbonate; thiocyanates and the other constituents of prussiate "metal" are without influence.

M. J. S.

Estimation of Sugar in Blood. By J. Seegen (*Chem. Centr.*, 1890, ii, 478—479; from *Centr. Physiol.*, **4**, 217—222).—The author has found that if, in the estimation of sugar in blood, the coagulum, caused by the addition of iron acetate, be not thoroughly and repeatedly pressed and washed, considerable quantities of sugar may be retained by it, although he has not found the error to be nearly so great as stated by Schenk and by Röhmann. In his first experiments, 5—8 per cent. was retained, and he considers that the sugar may be entirely washed from the coagulum independently of any choice of precipitating agent. J. W. L.

Examination of Oils, Fats, and Allied Substances. By T. T. P. B. Warren (*Chem. News*, **62**, 125; 179—180).—The sulphur chloride test recommended in various communications by the author indicates the character but not the probable quantity of the oils in a mixture; it is, therefore, now suggested to ascertain the latter factor by taking the iodine absorptions, with Hubl's reagent, of the individual constituent oils as well as of the mixture, and from the data obtained to determine the proportions present, for which purpose methods of calculating are described. D. A. L.

Estimation of Formic Acid in presence of Acetic and Butyric Acids. By A. Scala (*Gazzetta*, **20**, 393—396).—The liquid containing the formate is weighed out into a deep beaker, an excess of a saturated solution of corrosive sublimate added, the whole covered with a clock glass and heated for two hours on the water-bath. The precipitated calomel is collected on a weighed filter, washed with warm water, dried at 100°, and weighed. When the acid is present in the free state, it is neutralised before proceeding as above. This method gives trustworthy results, and is very sensitive, formic acid precipitating more than 10 times its weight of calomel.

S. B. A. A.

Modification of Jaffé's Indican Test. By F. Obermeyer (*Chem. Centr.*, 1890, ii, 273—274; from *Centr. Physiol.*, **4**, 155).—The author precipitates the urine with plumbic acetate, avoiding too large an excess, filters through a dry filter, agitates the filtrate with an equal volume of fuming hydrochloric acid, in which 2 to 4 parts of ferric chloride are dissolved in 1000 parts, and extracts finally with chloroform. The indigo produced by the oxidation of the indican may then be determined colorimetrically in the chloroform solution. Ferric chloride has the great advantage over others, as an oxidising agent of indican, that it does not affect the indigo produced. J. W. L.

General and Physical Chemistry.

Circular Polarisation of certain Tartrate Solutions. By J. H. Long (*Amer. J. Sci.* [3], **40**, 275—283; compare Abstr., 1890, 313).—The specific rotation of potassium antimony tartrate is considerably reduced by the admixture of carbonates, borates, phosphates, or acetates in amounts insufficient to produce immediate precipitation. Investigation of this behaviour leads to the conclusion that on mixing solutions of alkaline phosphates, acetates, carbonates, or borates with the tartrate in the cold, there is probably first formed a temporarily stable antimony salt, with a corresponding amount of alkaline tartrate. The observed rotation is due to this plus that of the unchanged potassium antimony tartrate.

The specific rotation of potassium ammonium tartrate is but slightly affected by the presence of ammonium or potassium salts, but is considerably diminished by the addition of a sodium salt. This behaviour may also be explained on the general hypothesis of replacement in the tartrate molecule by excess of inactive salts.

H. C.

Phosphorescence of Lithium Compounds in Vacua, and Spectra of Coated Terminals. By E. E. Brooks (*Chem. News*, **62**, 239).—Various lithium salts and minerals exhibited the following phosphorescence phenomena and continuous spectra showing a concentration of light in certain parts, when examined by Crookes' method in the negative discharge in a vacuum:—Sulphate, a bright lilac-blue; phosphate, bright, light Cambridge blue, when fused with sodium carbonate the colour became bright emerald-green, and, unlike the other cases, the glow was prolonged for a second or two after the circuit was broken; chloride, moderately brilliant, pale lavender-blue; fluoride, moderately brilliant, very light flesh-colour; silicofluoride, deep blue with darker spots, not so brilliant as the sulphate; spodumene, golden-yellow; lepidolite, very brilliant, deep-red, with traces of blue; petalite, very brilliant, rich yellow; amblygonite, trace of white glow; the nitrate, carbonate, hydroxide, and rubellite and indicollite did not phosphoresce; but the nitrate, fused in a glass tube, produced an opaque, enamel-like appearance at surfaces of contact, by which the inherent yellowish phosphorescence of the German glass became yellower.

By coating with, or simply placing on, aluminium or platinum negative terminals, lithium, thallium, sodium, calcium, or barium salts, and submitting them to a discharge in a vacuum of moderate tenuity, the flame spectra of the respective metals were obtained; other metals gave very faint spectra, or even none, with the 1-inch-spark coil employed. These spectra disappear in high vacua.

D. A. L.

Crystalline Liquids. By O. Lehmann (*Ann. Phys. Chem.*, **41**, 525—537).—The author has drawn attention to the fact that certain liquids exist which behave optically as if they had a crystalline structure (Abstr., 1890, 106). These liquids are chemically homogeneous, and the anisotropy is not produced by external force. He now asks the question whether isotropic liquids are non-crystalline, or whether they belong to the regular system, and concludes that in view of the very general miscibility of liquids they are non-crystalline, for otherwise they would only have the power of mixing with isomorphous substances. This conclusion he supports by experiments on the miscibility of crystalline liquids with each other and with solid crystals. Liquid crystals, when heated between cover glasses slightly above the point where they pass into ordinary liquids, retain on cooling the original direction of their optical axes, owing probably to condensation and consequent higher "melting" point of a layer on the surface of the glass. Isomorphous liquid crystals exhibit the phenomena of diffusion, and thus the capability of solids to form mixed crystals appears to correspond exactly with the process of mixing or diffusion in liquids (compare van't Hoff, Abstr., 1890, 1044). J. W.

Passive State of Iron and Steel. By T. ANDREWS (*Proc. Roy. Soc.*, **48**, 116—125).—Steel magnetised by hand or by a coil exhibits a small E.M.F., almost always positive with respect to non-magnetised steel, when both are immersed in nitric acid of sp. gr. 1·42 at the ordinary temperature. As the temperature is raised, the E.M.F. varies somewhat, but remains small, not exceeding 0·03 volt. At about 90°, however, the magnetised steel is attacked violently by the acid, and the E.M.F. rises suddenly to as much as 0·3 volt.

J. W.

Effect of Pressure on the Electrical Conductivity of Liquids. By C. BARUS (*Amer. J. Sci.* [3], **40**, 219—222).—For commercial mercury subjected to pressures between 10 and 400 atmos. isothermally, $-\delta R/R = 30 \times 10^{-6}\delta P$, where $\delta R/R$ is the decrement of the specific electrical resistance R, corresponding with the pressure increment δP. If v is the volume, then from the results of Grassi and others, $-\delta v/v = 3 \times 10^{-6}\delta P$, and hence $\delta R/R = 10\delta v/v$. If θ be the symbol of temperature, the following approximate results apply, isopiestically, at ordinary temperatures and pressures: $\delta R'/R' = 800 \times 10^{-6}\delta\theta$, and $\delta v/v = 180 \times 10^{-6}\delta\theta$. Hence $\delta R'/R' = 4{\cdot}4\ \delta v/v$, where R′ refers to electrical resistance considered in its thermal relations. For a concentrated solution of zinc sulphate subjected to pressures from 10 to 400 atmos., similar expressions apply with somewhat less accuracy.

Expressing the results graphically, the pressures in atmospheres or volume decrements per unit of volume are found to be linear functions of the corresponding decrements or increments of electrical resistance per unit of resistance. The curves for thermal change of resistance $\delta R'/R'$ coordinated with volume decrement are also rectilinear. In order to bring the compression loci into coincidence with the thermal loci, the former must be rotated in each case around the origin in a direction contrary to the hands of a watch. The angle of rotation is considerably greater for zinc sulphate solution than it is for mercury. From this, follows the remarkable result that, both in the case of the metal and of the electrolyte, the effect of isothermal compression is a decrement of resistance nearly proportional to pressure, and by deduction, that the immediate electrical effect of rise of temperature, $\delta R'/R' - \delta R/R$, is a decrement of specific resistance, both in the case of the metal and of the electrolyte. This points out an inherent similarity between the metallic and the electrolytic conduction in this instance. H. C.

Electrical Conductivity of Boric Acid Solutions in Presence of Dulcitol. By G. MAGNANINI (*Gazzetta*, **20**, 441—448).—The author has applied his new method of studying the constitution of solutions (see Abstr., 1890, 1357) to the investigation of the molecular composition of the compounds existing in solutions of boric acid and dulcitol. The variations of the molecular conductivity of boric acid solutions in presence of dulcitol are precisely of the same character as those which occur in presence of mannitol, with this difference, however, that from the observed values of the conductivity in the case of dulcitol, no simple relation for the molecular composition of the electrolytic compound or compounds can be calculated. This renders it probable that several compounds of boric acid and dulcitol exist together in the solution. S. B. A. A.

Determination of Boiling and Freezing Points by means of the Platinum Thermometer. By E. H. GRIFFITHS (*Proc. Roy. Soc.*, **48**, 220—225).—Eight thermometers, varying somewhat in construction, were compared. The best form was found to be the following:—A coil of fine platinum wire is wound on a roll of asbestos paper, and slipped into a thin tube of hard glass. Thick platinum wires run from this coil to the top of the instrument, and the unimmersed portion of the stem is surrounded by the outer tube of a condenser, through which tap-water is kept flowing. The diameter is less than 3/16ths of an inch, and the length about 18 inches. The instruments were graduated at the boiling points of water, naphthalene, benzophenone, and sulphur, and the freezing point of water. From the determinations of the boiling points of various substances, it was found that although the curves for the different thermometers vary considerably in form, intermediate temperatures deduced from them are in practical agreement (less than 0·1°) up to 500°.

J. W.

Heat of Combustion of Organic Compounds. By F. STOHMANN (*Zeit. physikal. Chem.*, **6**, 334—357).—In this paper are collected and systematically arranged the heats of combustion of over 400 organic compounds. The tables include all the determinations made from 1852 until August, 1890, with the exception of the experiments of Frankland, Ramsay, von Rechenberg, and Danileffski. Many hitherto unpublished determinations by the author and his pupils are also included. In the various columns are given the heat of combustion per gram in small calories; the heat of combustion per gram-molecular weight in great calories (both at constant pressure and constant volume); the heat of formation in great calories; the observer; and the reference to the original source. In calculating the heats of formation, the author assumes the following heats of combustion:—C, 94 Cal.; H_2, 69 Cal.; and S, 69·3 Cal. J. W.

Relations of the Heats of Combustion of Solid Bibasic Acids to those of the Gaseous Hydrocarbons. By F. STOHMANN (*J. pr. Chem.* [2], **42**, 248—259; compare Abstr., 1889, 1096, and Abstr., 1890, 100).—If A is the heat of combustion of any bibasic acid, and B that of the gaseous hydrocarbon from which it is derived, then the ratio A/B is practically a constant. A mean value for this constant obtained from the determinations of the heats of combustion of 22 different acids is 0·97692. Hence, if the heat of combustion of a molecule of a gaseous hydrocarbon is taken as unity, that of the corresponding bibasic acid will be 0·97692, or the heat of combustion of the hydrocarbon is obtained by dividing that of the acid by 0·97692. A comparison between numbers thus calculated and those observed shows a very satisfactory agreement.

The difference B − A is equal to the sum of two numbers x and y, the first of which is the loss of heat in the passage of the hydrocarbon from the gaseous to the solid condition, and the second the heat evolved in the conversion of the solid hydrocarbon into the corresponding acid. In some cases x is already known, and for others it may be calculated without serious error on the assumption that the heats of fusion and vaporisation of unit weight of all hydrocarbons are the same. The value of x being known, y the heat of formation of the acid from the hydrocarbon is then easily calculated.

The following table gives values of y for different acids calculated by the above method:—

	y. Cal.	K.		y.	K.
Malonic acid	2·5	0·17100	Fumaric acid	9·5	0·09300
Methylmalonic acid	1·7	0·08700	Phthalic acid	5·7	0·12100
Ethylmalonic acid	5·5	0·12700	Isophthalic acid	8·5	0·02870
Dimethylmalonic acid	8·1	0·07700	Salicylic acid	2·8	0·10200
Succinic acid	9·7	0·00665	Metahydroxybenzoic acid		
Methylsuccinic acid	8·2	0·00860		3·3	0·00867
Ethylsuccinic acid	7·4	0·00860	Parahydroxybenzoic acid		
Glutaric acid	6·2	0·00475		6·4	0·00286
Pimelic acid	8·1	0·00357	α-Naphthoic acid	1·0	0·02040
Adipic acid	10·7	0·00371	β-Naphthoic acid	4·2	0·00678
Maleïc acid	3·3	1·17000			

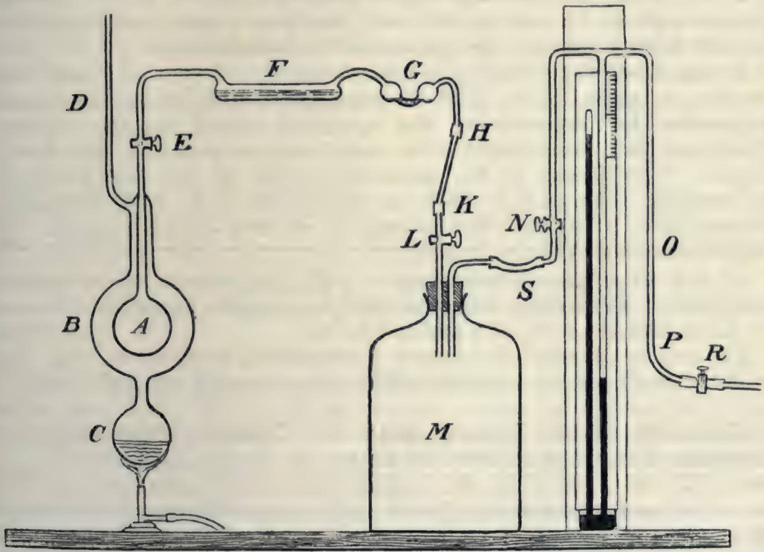
In the second column of the table, are given the values of Ostwald's affinity coefficients, between which and the heats of formation there is an evident relation, for acids of similar constitution the affinity coefficient being smaller the greater the heat of formation. Methylmalonic acid occupies an exceptional position in the malonic acid series. By analogy with the other acids of this series, the heat of formation should be between 2·5 Cal. and 5·5 Cal., and the affinity coefficient between 0·171 and 0·127. Instead of this, the numbers are 1·7 Cal. and 0·087.

H. C.

Compressibility of Mixtures of Air and Carbonic Anhydride. By U. LALA (*Compt. rend.*, **111**, 819—821).—The author has investigated the compressibility of mixtures of air and carbonic anhydride containing 11 to 56·92 per cent. of the latter, at pressures extending to 1613·96 cm. of mercury. When the proportion of carbonic anhydride does not exceed 22 per cent., the compressibility lies between that of air and carbonic anhydride, and is, at first, nearer to that of air, but approaches more closely to that of carbonic anhydride as the pressure increases. The greater the proportion of carbonic anhydride, the lower the pressure at which the compressibility becomes equal to that of carbonic anhydride alone. As the proportion of this gas increases, the compressibility becomes greater than it would be if no air were present, but beyond a certain point it decreases and tends to revert to the compressibility of pure carbonic anhydride.

C. H. B.

Experiments on Vapour Density. By E. P. PERMAN (*Proc. Roy. Soc.*, **48**, 45—59).—This investigation was undertaken mainly to ascertain if bromine dissociates at low pressures and moderate temperatures. The apparatus employed is figured in the accompanying cut. *A* is a glass globe of known capacity (about ½ litre) blown inside a larger globe, *B*. The liquid which produces the vapour-jacket is boiled in *C*, and condensed in *D*, which may be specially cooled if necessary. *F* is a tube containing a liquid to absorb the bromine vapour, a few drops being also introduced into



the bulb-tube *G*. *M* is an air reservoir, and *O* a pressure gauge, the tube *P* being attached to a water-pump.

A is first exhausted, and then there is introduced into it a little liquid bromine, air being excluded. The tube above *E* is fused on to *F*, the liquid in *C* boiled, and the bromine allowed gradually to blow out over the potash solution in *F*. The tube above the globe must be heated gently with a Bunsen flame. The apparatus is now exhausted as far as possible, the stopcock *E* turned off, the tube above cracked and removed, more bromine admitted as at first, the tube fused together again, and the bromine driven out as before until the vapour in *A* has the atmospheric pressure at the temperature of the boiling liquid in *C*. The absorption-tube *F* is then filled with strong solution of potassium iodide, and the whole apparatus connected up as in the figure. *M* is exhausted to the requisite degree, and the pump cut off by the screw-clip *R*. Bromine vapour is allowed to escape from *A* by cautious manipulation of the stopcock *E* until equilibrium is attained. The pressure is then read off, the stopcock *L* closed, and the contents of the absorption-tube washed into a stoppered bottle to be afterwards titrated with thiosulphate. The experiment is then repeated at lower pressures until the series is complete.

By adding together the residual quantity of bromine and the quantities removed, the weight of bromine in the globe at each pressure is found, and as the volume occupied is already known, all data required are available.

It was found that at temperatures ranging from 15° to 280°, and at pressures from 15 mm. to 760 mm., bromine vapour exhibited the normal density without any indication of dissociation.

Iodine, when vaporised in a similar apparatus, did not yield constant results, so experiments with it were conducted by means of an apparatus for determining the speed of sound in the vapour. Finely-divided precipitated silica was used to ascertain the wave-length. The density of the saturated vapour at 132° was found to be normal. The author finds (in contradiction to J. J. Thomson, Abstr., 1887, 1013) that the passage of electric sparks through the vapour does not alter its density.

A few experiments were made with the vapour of sulphuric anhydride. The author considers that his results prove the formula of this substance to be SO_3 and not S_2O_6.

The vapour density of aqueous hydrochloric acid shows that the acid and water do not combine at the temperature employed (132°).

J. W.

Variation of the Density with the Concentration of Weak Aqueous Solutions of Certain Salts. By J. G. MacGregor (*Chem. News*, **62**, 223—224, 232—234).—The densities of the various solutions were, in these experiments, determined in a specific gravity bottle at 20°, and, as a rule, at least two solutions of different strengths of each salt were prepared from weighed quantities of the recrystallised pure crystalline salt of commerce and weighed quantities of water, the intermediate solutions being obtained by dilution. With ferrous sulphate, however, all solutions were made directly from the salt and water; in this case, also, air was eliminated from the water as far as possible by boiling.

In all the salts tested, in concentrations varying from 1 per cent. to about 5 per cent. of anhydrous salt, the excess of density of a solution over that of water at the same temperature is directly proportional to the percentage of salt in the solution, and may be represented symbolically by the equation

$$\mathrm{D}t = d_t + kp,$$

in which D_t and d_t are the densities at the same temperature t of a solution and of water respectively, p the percentage of anhydrous salt in the solution, and k a constant for all sufficiently dilute solutions of any one salt. Data are furnished showing the close agreement between the numbers calculated from the formula and those obtained from actual observations. In the following table, the value of k is given, and the maximum observed concentration up to which it holds good for each salt.

Salt.	*t*.	*k*.	Maximum concentration per cent.	Observer.
$ZnSO_4$	20·0°	0·0103918	3·0	MacGregor.
$MgSO_4$	20·0	0·0106324	2·0	,,
$MgSO_4$	23·0	0·0098176	between 2·0 and 2·5	Schiff.
$FeSO_4$	20·0	0·0099436	above 2·6	MacGregor.
$CdSO_4$	18·0	0·0097329	about 3·0	Grotrian.
$CuSO_4$	18·0	0·0098427	below 2·0	Gerlach.
$Al_2(SO_4)_3$	12·5	0·0092083	2·5	Hassenfratz.
$AlK(SO_4)_2$	20·0	0·0095187	at least 1·7 possibly 2·5	MacGregor.
K_2SO_4	15·0	0·0081600	2·5	Gerlach.
K_2SO_4	12·5	0·0085950	2·5	Hassenfratz.
Na_2SO_4	15·0	0·0091875	4·0	Ostwald.
Na_2SO_4	15·0	0·0091267	4·0	Gerlach
KHO	18·0	0·0093717	over 5·0	Thomsen.
NaHO	18·0	0·0145630	about 2·0	Thomsen.

The formula seldom applies to concentrations below 1 per cent., exceptions being magnesium, copper, and potassium aluminium sulphates.

D. A. L.

Dissociation Hypothesis of Arrhenius. By J. TRAUBE (*Ber.*, **23**, 3519—3530).—The author raises a number of objections to the hypothesis of Arrhenius of the dissociation of electrolytes in dilute aqueous solution (Abstr., 1888, 896). The hypothesis contradicts our ordinary conceptions of chemical affinity, since even the most stable compounds are assumed to dissociate when dissolved in water. All explanations of reactions in solution based on the assumption of a so-called nascent condition become impossible under the new hypothesis. To explain the fact that the ions which are assumed to exist in the free state in aqueous solutions cannot be separated from one another by diffusion, the further assumption is made that the ions are endowed with charges of opposite sign, and are, in consequence, so dependent one on another that they cannot be separated without the application of energy from the outside. This is, however, to assume a dissociation where none really occurs. According to the hypothesis, the colour of any particular ion in solution should always be the same, whereas an atom of iron in the thiocyanate is red, in Prussian blue is blue, in ferrous sulphate is green, and in ferric chloride is yellow. The additive properties of dilute solutions, which Arrhenius regards as of so much importance in support of the hypothesis, are rather to be looked on as a weak point. For were the hypothesis correct, *all* the properties of dilute solutions would be of an additive nature, and this is by no means the case. The freezing point reduction of a mixed solution is either equal to or less than the sum of those of its constituents, according as there is no action between the salts or the formation of a double salt. On the dissociation hypothesis, the former only would be the case. The hypothesis also contradicts in every way the hydrate theory, ignoring the fact that from the properties of solutions the existence of hydrates has been predicted which have subsequently been obtained in the free state. We should be compelled to assume that even in solutions of 10 per cent. to 15 per cent. concentration, salts exist in a dissociated condition, and if we accept the Arrhenius reasoning, that in a 65 per cent. solution of silver nitrate this salt is completely dissociated.

Ostwald (Abstr., 1888, 1020, 1142) applies the laws of gaseous dissociation to electrolytes, but the formula he obtains, $m^2/(1 - m)v = C$, which should be applicable to all binary electrolytes, only holds for organic acids of low conductivity. Although, therefore, the formula holds for some hundreds of acids, there are an equally large number of compounds to which it is absolutely inapplicable. The application of the gaseous laws by Arrhenius to electrolytes leads to the conclusion that the dissociation is attended in some cases with a development of heat, a result which cannot be reconciled with the idea that energy is required to separate the ions from one another. The phenomena of electrolytic conduction are opposed to the dissociation hypothesis. For since many indifferent organic compounds have a molecular conductivity, which like that of the acids decreases with the concentration, it would be necessary to assume for these also an electrolytic dissociation, which, however, is impossible. In the same way, all the abnormal results for the osmotic pressure, and lowering of the freezing point of organic compounds, would have to be taken as indicating that these also undergo electrolytic dissociation.

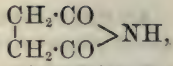
Objections are raised to Arrhenius' method of calculating the value of i from the conductivity (*loc. cit.*). The values of α are calculated for solutions containing 1 gram of the dissolved substance in a litre of water. The freezing point determinations, on the other hand, apply to normal or half-normal solutions. The error, therefore, in the latter series of numbers must be at least 20 per cent. The value $\alpha = 0$ is assumed for non-electrolytes, but the author cannot see any reason why the law of Kohlrausch $\lambda = u + v$ should be applied at all to non-electrolytes. H. C.

Surface Tension of the Halogens. By A. A. Trussewitsch (*Zeit. physikal. Chem.*, **6**, 360—361).—The author, in this preliminary communication, gives the results he obtained from measurement of the capillary elevation of bromine and liquid chlorine. He finds for bromine $\gamma = 4{\cdot}11$, and for chlorine $\gamma = 2{\cdot}72$. J. W.

Influence of Mass on Chemical Processes. By F. Kehrmann (*J. pr. Chem.* [2], **42**, 134—142).—The author gives some further instances in support of the view that he put forward in a former paper (Abstr., 1890, 484), that not only the laws of chemical affinity, but also the atomic or molecular weight of the replacing atom or radicle dominates or directs the position which it takes up in any compound. The above assumption serves to explain the fact that many compounds, such as benzildioxime, are capable of existing in stereochemically different forms, whereas other compounds of analogous constitution, such as diacetyloxime, exist only in one form.
H. C.

Affinity Constants of Organic Acids, &c. By R. Bader (*Zeit. physikal. Chem.*, **6**, 289—318).—The author, in this paper, communicates his determinations of the dissociation constants of some 60 organic substances of acid character. The chief compounds investigated are the hydroxybenzenes, their derivatives, and certain cyanamide compounds.

The mono- and poly-hydroxybenzenes are extremely feeble acids, so much so that it is impossible to obtain a constant for them at all. When alkyl radicles, however, are introduced into the benzene nucleus, the acid properties increase markedly, the cresols, for example, giving definite though still very small constants. The introduction of a chlorine atom exerts no great influence on the phenols; the nitro-group, on the other hand, is extremely active, nitrophenol and the dinitrophenols being moderately strong acids. The position of the substituent groups with regard to the hydroxyl here plays a great part in determining the strength of the compound. Trinitrophenol (picric acid) is quite comparable to the mineral acids. Nitrodihydroxy-derivatives are stronger than the corresponding nitromonohydroxy-compounds, but are still dissociated only as monobasic acids.

Cyanamide in aqueous solution scarcely conducts electricity at all, is thus feebly dissociated, and shows no distinct acid properties. Its derivatives of the type $CN{\cdot}NHR'$, where R' is a univalent acid radicle, are, however, in many cases strong acids, being usually much more powerful than the corresponding carboxylic acids themselves. Thus, whilst acetic acid has the constant $K = 0{\cdot}0018$, acetylcyanamide, $CN{\cdot}NH(C_2H_3O)$, has $K = 0{\cdot}015$. When the substituting radicle is that of a sulphonic acid, the resulting substance, though acid, is by no means so powerful as the corresponding compound derived from a carboxylic acid: for example, we have for $CN{\cdot}NH(C_6H_5{\cdot}CO)$, $K = 0{\cdot}186$; but for $CN{\cdot}NH(C_6H_5{\cdot}SO_2)$, $K = 0{\cdot}0013$. The replaceability of the hydrogen atom of the imido-group is evidently conditioned by the simultaneous presence of the cyanogen group and an acid radicle in the molecule. An acid radicle alone is insufficient to impart strongly acid properties to the group NH; succinimide,  $\begin{matrix}CH_2\cdot CO\\ | \\ CH_2\cdot CO\end{matrix}\!\!>\!NH$, for instance, being practically a non-conductor of electricity in aqueous solution.

Other acids investigated were β-naphthoic acid and its reduction products; α-thiophenic acid (stronger than benzoic acid); tetrahydro-α-thiophenic acid; phenylglyoxylic acid (very powerful) and its ketoxime; isocinnamic acid (much stronger than ordinary cinnamic acid); dimethylglutaric acid; and α- and γ-truxillic acids.

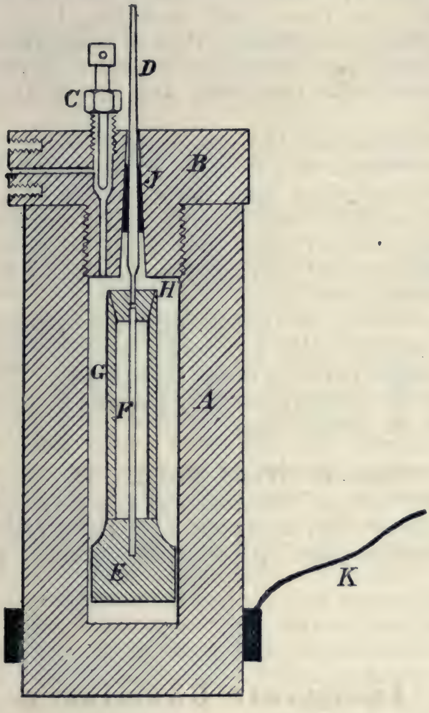
J. W.

Coefficient of Mineral Condensation in Chemistry. By T. S. Hunt (*Amer. Chem. J.*, **12**, 565—585).—Solid or liquid mineral species (including under the designation of minerals all distinct forms of unorganised matter) are formed by intrinsic condensation or polymerisation from simpler chemical species, often themselves gaseous. There is at present no method of fixing the amount, or, in other words, of determining the coefficient, of the condensation, often very considerable, which results in the production of such mineral species. The author proposes, however, to do this by assuming that for all species, whether gaseous, liquid, or solid, the molecular weight varies as the density, taking that of hydrogen under normal conditions as the unit. Dealing with solids and liquids, the density of which is referred to water as unity, it will be necessary to multiply this density by about 21400, the number expressing the density of liquid water with respect to hydrogen, in order to obtain the molecular weight of a substance in the solid or liquid state. Dividing the number so obtained by the ordinarily accepted molecular weight, deduced chemically or from the gaseous density, we get the coefficient of mineral condensation. Thus for quartz, $SiO_2 = 60$, the density of which is 2·65, the coefficient of mineral condensation will be $2{\cdot}65 \times 21400/60 = 945$ approximately, and for other substances it may be calculated in like manner.

The coefficient of mineral condensation expresses the degree of polymerisation necessary in the conversion of the simple gaseous chemical species into the liquid or solid mineral species. The author quotes a number of facts in favour of the view that solid molecules are built up by condensation from the gaseous molecules, and that the above reasoning is therefore perfectly justifiable. All the facts that have up to the present been ascertained with regard to the molecules of solid substances point to their being of great complexity, as would be the case if the views above explained are correct.

H. C.

Reactions at High Temperatures and Pressures. By W. Hempel (*Ber.*, **23**, 3388—3392).—The author describes an apparatus consisting of a steel cylinder A, containing a porcelain tube G in which the substance under examination is placed. Down the middle of the tube, a thin rod of carbon F passes and fits into a carbon block E; it may be heated by the electric current, passed by means of the copper wires D and K; the head B of the steel cylinder screws on air-tight, and provision is made for pumping in gas through the valve C, until the desired pressure is obtained. Experiments with this apparatus show that the quantity of cyanides obtained from carbon, nitrogen, and alkaline oxides increases as the pressure becomes greater, potassium cyanide being much more readily formed than barium cyanide. The production of boron nitride from boric anhydride, carbon, and nitrogen follows the same rule. J. B. T.



Apparatus for Fractional Distillation in a Vacuum. By H. Schulz (*Ber.*, **23**, 3568—3570).—The apparatus described in this paper resembles in many respects that recently described by H. Wislicenus (this vol., p. 146), but differs from it, inasmuch as the bell-jar covering the vessels for the collection of the distillate is the part which is made to rotate. It is very simple in construction, and can readily be made of any size, and is, therefore, suitable for technical purposes. H. G. C.

Error in the Principle of the Ordinary Exsiccator. By W. Hempel (*Ber.*, **23**, 3566—3568).—In the ordinary exsiccators, the material used for absorbing the moisture is always placed at the bottom, the result of which is that diffusion of dry air takes place very slowly, owing to the fact that dry air is heavier than moist air at the same temperature. If the drying material be placed above the substance which is to be dried, a much more rapid evaporation will take place, the dried air falling to the bottom, and thus causing rapid currents within the apparatus. To determine the difference in the desiccating action, two dishes, each containing 10 c.c. of water, were placed in two similar exsiccators, the one being above and the other below the dish containing the sulphuric acid. In the first case, the water took nine days to evaporate, and in the second only three days.

The author recommends the employment of an ordinary bell-jar exsiccator, in which the dish of drying material is fixed as high as possible on an iron tripod, and the substance to be dried placed underneath. If sulphuric acid is employed, it is advisable to place in the liquid large pieces of glass, porcelain, or pumice stone. The last named substance must previously be boiled with sulphuric acid to remove the chlorides it contains.

The drying action may be further increased by cooling the highest portion of the bell-jar with a freezing mixture, which causes the formation of stronger currents inside the exsiccator. Notwithstanding the presence of the sulphuric acid, the moisture separates out at the coolest places in the form of snow. H. G. C.

Absorption Plates of Wood Wool. By W. CAMERER (*Zeit. anal. Chem.*, 1890, 576).—This material is a very advantageous substitute for the porous clay and plaster of Paris plates hitherto used for drying precipitates, &c. A coating of cellulose gives a smoother surface. M. J. S.

Inorganic Chemistry.

Molecular Weights of Sulphur, Phosphorus, and Iodine in Solution. By J. HERTZ (*Zeit. physikal. Chem.*, **6**, 358—359).—Phosphorus dissolved in benzene gives a depression of the freezing point corresponding with the formula P_4. The numbers obtained with sulphur dissolved in naphthalene point to the existence of molecules S_8, in accordance with the results obtained by Beckmann, who employed carbon bisulphide as solvent (Abstr., 1890, 447). The red solution of iodine in naphthalene yields numbers corresponding with the molecule I_2. J. W.

Action of Metals on Sulphuric Acid. By A. DITTE (*Ann. Chim. Phys.* [6], **19**, 68—92).—The author has investigated the action of a number of metals on sulphuric acid of different degrees of concentration and at various temperatures; the following general conclusions may be drawn from the results of the experiments:—

The metals attacked by sulphuric acid can be classed in two groups.

The one contains those metals which are acted on only when the acid is concentrated and hot; the reaction is very regular in all cases, and sulphurous anhydride alone is evolved, no secondary reactions taking place. To this class belong silver, mercury, copper, lead, and bismuth.

The second group embraces those metals which are acted on more or less readily by sulphuric acid of all degrees of concentration. The most constant product of the reaction is hydrogen, this gas being always evolved in the cold, and almost always at a high temperature also; when the temperature is not very high, hydrogen is the sole gaseous product, whatever the degree of concentration of the sulphuric acid employed. Sulphurous anhydride is only produced when the acid is hot and concentrated; the temperature at which the evolution of sulphurous anhydride commences varies with the metal employed, and, generally speaking, its quantity increases in proportion to the rise of temperature, the quantity of hydrogen decreasing to a proportionate extent, and sometimes, when the temperature is very high, disappearing altogether. When the concentration of the sulphuric acid decreases, the formation of sulphurous anhydride also decreases, so that, even at a high temperature, it is not obtained free from hydrogen; when a certain degree of dilution of the acid is reached, sulphurous anhydride ceases to be formed. Between certain limits of temperature and concentration, which vary with the nature of the metal employed, the action of sulphuric acid gives rise to a mixture of hydrogen and sulphurous anhydride, so that by choosing a suitable temperature and an acid of suitable strength, a mixture of the two gases, in any required proportion, could be obtained.

This is true in the case of metals, like magnesium, which only yield hydrogen when treated with sulphurous acid, as the reducing action of the hydrogen on the sulphurous acid under the conditions of the experiment may be neglected. When, however, the metal employed decomposes sulphurous acid, yielding a sulphide, secondary reactions set in, and hydrogen sulphide is formed; in such cases, larger or smaller quantities of this gas are formed according as the action of the metal on the sulphurous acid is rapid or slow, and according as the sulphide produced is readily or slowly acted on by the sulphuric acid. The hydrogen sulphide thus produced decomposes, and is itself decomposed by, some of the sulphurous acid, and it also reduces the sulphuric acid causing a deposition of sulphur, which, in its turn, acts on the sulphuric acid. When, however, the metal is treated with sulphuric acid under such conditions that sulphurous acid is not produced, the formation of hydrogen sulphide and other secondary reactions cease, and pure hydrogen is evolved. To the second of these two groups belong magnesium, manganese, nickel, cobalt, iron, zinc, cadmium, aluminium, tin, thallium, and probably also the alkali metals. In the case of the last named, it was only possible to study the behaviour with sulphuric acid in the cold, and under these conditions hydrogen is evolved, but, considering the close relationship between the alkaline metals and thallium, it is very probable that, like the latter, they would yield sulphurous anhydride on treatment with sulphuric acid at a high temperature.

F. S. K.

Selenites. By BOUTZOUREANO (*Ann. Chim. Phys.* [6], **18**, 289—351).—The author has prepared the following selenites:—

SELENITES OF BIVALENT METALS.—*Basic selenites*:—$2CuO,SeO_2$, clinorhombic. *Normal selenites*:—$MgO,SeO_2 + 6H_2O$, cubic. $MgO,SeO_2 + 2H_2O$, clinorhombic. ZnO,SeO_2, orthorhombic. CdO,SeO_2, orthorhombic. $3(CuO,SeO_2) + H_2O$, clinorhombic. $3(CoO,SeO_2) + H_2O$, clinorhombic. $2(NiO,SeO_2) + H_2O$, orthorhombic. *Acid selenites*:—$MgO,2SeO_2$, rhombohedric. $ZnO,2SeO_2 + 3H_2O$, clinorhombic. $2CdO,3SeO_2 + H_2O$, clinorhombic. $CdO,2SeO_2$, orthorhombic. $CuO,2SeO_2 + H_2O$, clinorhombic. $CuO,2SeO_2 + 2H_2O$, clinorhombic. $CuO,2SeO_2 + 4H_2O$, clinorhombic. $2(MnO,2SeO_2) + H_2O$, clinorhombic. $MnO,2SeO_2 + 5H_2O$. $CoO,2SeO_2 + 3H_2O$, clinorhombic. $CoO,2SeO_2$, clinorhombic.

SELENITES OF QUADRIVALENT METALS.—*Basic selenites*:—$Mn_2O_3,2SeO_2$, clinorhombic. $Fe_2O_3,2SeO_2$, clinorhombic. *Normal selenites*:—$Fe_2O_3,3SeO_2 + 10H_2O$, clinorhombic. $Fe_2O_3,3SeO_2 + 3H_2O$, cubic. $Fe_2O_3,3SeO_2 + H_2O$, clinorhombic. $Al_2O_3,3SeO_2 + 7H_2O$, hexagonal. $Al_2O_3, 3SeO_2 + 3H_2O$, cubic. U_2O_3,SeO_2, cubic. *Acid selenites*:—$Fe_2O_3,4SeO_2 + H_2O$, orthorhombic. $Fe_2O_3,6SeO_2 + 2H_2O$, clinorhombic. $Al_2O_3,4SeO_2 + 3H_2O$, orthorhombic. $Al_2O_3,6SeO_2 + 2H_2O$, clinorhombic. $2(U_2O_3),3SeO_2 + 7H_2O$, clinorhombic.

AMMONIACAL SELENITES.—ZnO,SeO_2,NH_3, orthorhombic. CdO,SeO_2,NH_3, orthorhombic. $CuO,SeO_2,NH_3 + H_2O$, triclinic. Ag_2O,SeO_2,NH_3, triclinic.

With a few exceptions, the compounds given in the above list have not hitherto been prepared.

The most successful methods for preparing the salts and obtaining them in well-defined crystals were found to be (1) heating the amorphous or crystalline compounds in sealed tubes at 150—270° with water, or with a solution of selenious anhydride, or adding selenious anhydride to a solution of a salt already prepared and heating the mixture in sealed tubes; and (2) dissolving metallic carbonates in selenious acid and evaporating the solution.

The ammoniacal selenites were prepared by dissolving the selenites in ammonia and evaporating the solutions at the ordinary temperature or at 100°.

In estimating the selenium in the salts, except in the case of the salts of the sesquioxides, the best method was found to be the reduction of the selenious acid with sodium hydrogen sulphite in hydrochloric acid solution; the results are very satisfactory when care is taken to prevent the volatilisation of the selenious anhydride, and to ensure complete reduction. In the case of the selenites of the sesquioxides, attempts were made to determine the selenium by Rose's method, but as the results were not satisfactory, the salts were first boiled with a concentrated solution of sodium carbonate, and the selenious acid in the filtered solution estimated by reduction with sodium hydrogen sulphite as before. F. S. K.

Preparation of the Nitrogen Hydride N_2H_6. By E. J. MAUMENÉ (*Bull. Soc. Chim.* [3], **4**, 179—180; compare Abstr., 1889, 14).—By the dry distillation of ammonium platinochloride, the chloride

$N_2H_4Cl_2$ is obtained in six-sided, orthorhombic crystals which condense on the walls of the retort. T. G. N.

Hydrazine Hydrate and Haloïd Salts (Halogen Diammonium Compounds). By T. Curtius and H. Schulz (*J. pr. Chem.* [2], **42**, 521—549; compare Abstr., 1889, 340).—Hydrazine sulphate forms rhombic crystals, $a : b : c = 0{\cdot}74532 : 1 : 0{\cdot}82825$; observed faces $\infty\bar{P}\infty$, $0P$, $\bar{P}\infty$, $\check{P}\infty$, $\infty\check{P}2$, $2\check{P}2$; crystals tabular across $\infty P\infty$, colourless and clear; cryoscopic determination of its molecular weight, in water, gave 69·16, 62·871, and 60·705 respectively.

Hydrazine hydrate is best prepared by distilling a mixture of hydrazine sulphate (100 grams), potassium hydroxide (100 grams), and water (250 grams) in a silver retort provided with a silver condensing tube. The distillation is continued (5—6 hours) until the last drop has passed over, and the distillate (250 c.c.) is then fractionated, the fractions being best divided into below 101°, 101—104°, 104—117°, 117°—constant boiling point. After four fractionations, the hydrazine hydrate (36 grams) boils constantly at 119°.

Most of the properties of hydrazine hydrate have been already detailed (Abstr., 1889, 340); it is hygroscopic, and absorbs carbonic anhydride; it can be kept in closed vessels unchanged; it dissolves in water and alcohol, but not in ether, chloroform, or benzene; it solidifies in solid carbonic anhydride and ether, but melts again below −40°; it boils (739·5 mm.) at 118·5°; its sp. gr. at 21° is 1·0305; in its reactions with indicators it resembles ammonia. Determination of the vapour density of hydrazine hydrate, made by Hofmann's method at 100°, show that its molecule, under these conditions, is N_2H_4,H_2O; those made by Victor Meyer's method at 170°, and at atmospheric pressure, show that the molecule is dissociated under these conditions into N_2H_4 and H_2O; cryoscopic determinations show that the molecular weight of hydrazine hydrate in water is 68, agreeing with the formula $N_2H_4,2H_2O$.

Hydrazine hydrate which has been redistilled over barium oxide fumes in the air more strongly than the pure liquid, showing that it contains free hydrazine dissolved in it. When the hydrate is heated in a sealed tube with barium oxide at 170°, and the tube is subsequently opened, hydrazine (diamide) escapes as a white fume; experiments in this direction are still in progress.

The hydrazine haloïd salts are prepared either by mixing aqueous solutions of hydrazine hydrate and the halogen acid and evaporating, or by adding the acid to an alcoholic solution of the hydrazine hydrate, and subsequently adding ether, whereby the salt is precipitated. When hydrofluoric and hydrochloric acids are used, the salts $N_2H_4,2HR$ are obtained by both methods; with hydrobromic acid, the first method yields the salt $N_2H_4,2HBr$, and the second method the salt N_2H_4,HBr; with hydriodic acid, both methods yield the salt N_2H_4,HI.

The salts $N_2H_4,2HR$ crystallise in the regular system, and are isotropic in polarised light; they dissolve easily in water, but are nearly insoluble in alcohol. The salts N_2H_4,HR are easily soluble in water and in warm alcohol, from which they crystallise well. Both classes are insoluble in ether, benzene, &c.

Hydrazine dihydrofluoride (diammonium difluoride), $N_2H_4,2HF$, melts at 105°, and sublimes undecomposed in presence of excess of the salt. Hydrazine dihydrochloride has been already described (Abstr., 1887, 715); it can also be obtained by passing chlorine into hydrazine hydrate. *Hydrazine dihydrobromide*, $N_2H_4,2HBr$, melts at 195°: it can also be obtained by decomposing benzalazine (Abstr., 1889, 393) with hydrobromic acid. *Hydrazine dihydriodide*, $N_2H_4,2HI$, can only be obtained by decomposing benzalazine with fuming hydriodic acid; it is very hygroscopic, becomes brown on exposure to light, and melts at 220°.

Hydrazine monhydrochloride has already been described (Abstr., 1889, 340). *Hydrazine monhydrobromide*, N_2H_4,HBr, is prepared by adding bromine to hydrazine hydrate suspended in chloroform; it forms large, anisotropic, columnar crystals and melts at 80°. *Hydrazine monhydriodide*, N_2H_4,HI, may be obtained by adding iodine to an alcoholic solution of hydrazine hydrate; it melts at 127° and then explodes.

Trihydrazine dihydriodide, $N_6H_{12},2HI$, is obtained when iodine is added to a solution of hydrazine hydrate in a little alcohol until white crystals separate; it dissolves easily in water, and crystallises from alcohol in large, white needles which melt at 90° and are optically biaxial; when its aqueous solution is evaporated with hydriodic acid, it yields hydrazine monhydriodide.

Cryoscopic determinations of the molecular weights of the above salts show that in aqueous solution:—(1) the salts N_2H_4,HR have molecular weights which are half those expressed by their formulæ; (2) trihydrazine dihydriodide has a molecular weight which is one-fifth of that expressed by its formula; (3) the salts $N_2H_4,2HR$ have molecular weights which are one-fourth of those expressed by their formulæ (except that of $N_2H_4,2HF$, which is one-half that expressed by the formula). With regard to hydrazine sulphate, see above. These phenomena are to be explained by the dissociation of the salts in cases (1) and (2) into free molecules of N_2H_4 and HR, and in case (3) into molecules of NH_3 and R.

The author concludes with some speculations as to the constitution of hydrazine hydrate and trihydrazine dihydriodide. A. G. B.

Phosphorus Trifluoride. By H. Moissan (*Ann. Chim. Phys.* [6], **19**, 286—288; compare Abstr., 1885, 15 and 482).—Phosphorus trifluoride can be prepared by gradually adding phosphorus tribromide to zinc fluoride which is gently heated; the gas is washed with water, dried with pumice moistened with a little sulphuric acid, and collected over mercury. F. S. K.

Preparation of Phosphorus Oxyfluoride. By H. Moissan (*Bull. Soc. Chim.* [3], **4**, 260—262; compare Trans., 1889, 759).—Zinc carbonate is dissolved in excess of hydrofluoric acid, the solution is evaporated, and the zinc fluoride dried at 300° and placed in a brass tube, to which a bromine burette, containing slight excess of the calculated quantity of phosphorus oxychloride, and a leaden delivery tube are adapted by a paraffined cork. The leaden tube is connected to a brass tube cooled by a freezing mixture to −20°, and this leads to another tube containing zinc fluoride, which removes any traces of escaping oxychloride from the oxyfluoride. The phosphorus oxychloride is dropped slowly on to the zinc fluoride, the ensuing reaction being assisted by warming carefully at 40—50°, and the evolved gas is collected over mercury in glass vessels. The author determined the phosphorus contained in the gas in three instances as 29·2, 29·4, and 29·95 per cent., theory requiring 29·8 per cent., and the vapour density as 3·68, 3·69, and 3·71, theory requiring 3·63. T. G. N.

Arsenic Fluoride. By H. MOISSAN (*Ann. Chim. Phys.* [6], **19**, 280—286; compare Abstr., 1885, 121).—Arsenic trifluoride is formed when arsenious anhydride is treated with anhydrous hydrogen fluoride, and when arsenic chloride is warmed with lead or silver fluoride, but it is best prepared by heating a mixture of arsenious anhydride and calcium fluoride with excess of sulphuric acid, as described by Dumas (*Ann. Chim. Phys.* [2], **31**, 433).

Arsenic fluoride boils at 63° (750 mm.), and its density is 2·73 (compare MacIvor, *Chem. News*, **30**, 169, and **32**, 232). It solidifies at −8·5° to a mass of crystals. When exposed to a dull red heat in a glass vessel free from air, it is decomposed, yielding arsenious anhydride and silicon tetrafluoride. F. S. K.

Action of Hydrogen Sulphide on the Ortharsenates of the Alkali Metals. By W. McCAY (*Amer. Chem. J.*, **12**, 547—553; compare Brauner and Tomíček, Trans., 1888, **53**, 145).—The author finds that arsenic pentasulphide may be prepared by the decomposition of a strong solution of an alkali arsenate with hydrogen sulphide, and subsequent precipitation by the addition of a mineral acid, according to the method proposed by Berzelius; but that the operation is successful only under the following definite conditions:—In the case of dihydrogen alkali arsenates, the solution must be properly diluted and kept hot, and the hydrogen sulphide passed in excess and for a long time. In the case of the di- and tri-alkali arsenates, the hydrogen sulphide must be kept present in such large excess and passed for such length of time that there is no chance of the potassium thioxyarsenate, which is always formed in passing, in the wet way, from arsenic acid to thioarsenic acid, to split up into potassium arsenite and sulphur, or to escape subsequent conversion into the thio-salt. G. T. M.

Certain Forms of Carbon. By P. SCHÜTZENBERGER and L. SCHÜTZENBERGER (*Compt. rend.* **111**, 774—778).—When pure and dry cyanogen is passed through a porcelain tube at a cherry-red heat, it is only partially decomposed, and even at a bright-red heat the decomposition is very limited, the interior of the tube being covered with a thin, brilliant, blackish-grey coating, with a sub-metallic lustre resembling that of polished graphite. If, however, there is placed in the hot part of the tube some gas carbon with powdered cryolite sprinkled over the surface, the cyanogen decomposes completely into carbon and nitrogen, even at a cherry-red heat. The carbon separates in a bulky mass of very slender filaments, and, after a time, stops up the tube. Those portions in contact with the walls of the tube are more compact and somewhat elastic. It is friable, and leaves on paper a mark resembling that made by graphite, but not so bright. When a piece of aluminium was placed amongst the gas carbon, the carbon separated round it in non-elastic filaments, which could be compressed between the fingers into a mass resembling graphite.

The carbon deposited at a cherry-red heat was treated with nitric acid and potassium chlorate at 20—25° for 24 hours. The insoluble residue, after being washed and dried, forms a deep maroon-brown powder, which decomposes suddenly when heated, becoming incandescent and evolving carbonic anhydride and water. The properties of this product are not materially affected by a second treatment with acid and chlorate in the cold, but if the mixture is heated at 50—60° for several hours, a somewhat pale brownish-yellow powder is obtained, which deflagrates energetically when heated. A portion of the product is soluble in water, and repeated treatment with the oxidising mixture converts the whole of it into yellow, soluble compounds. The pale brownish-yellow, insoluble product has the composition, C, 56·2; H, 2·5; O, 41·3 = 100; and its formula is $C_{11}H_6O_6$, that of Brodie's graphitic acid being $C_{11}H_4O_5$. The maroon-brown product obtained at 20—25° has the composition of graphitic acid. The carbon obtained in presence of aluminium yields similar products.

The filamentous carbon obtained by the decomposition of cyanogen is not identical with any of the established forms of graphite or carbon, and may be taken as a new modification.

Gas carbon, when treated two or three times in the cold with a mixture of potassium chlorate and nitric acid, yields a blackish powder which deflagrates on heating. At 45—50°, it yields products similar to those obtained from cyanogen carbon. It follows that the property of yielding hydroxides which deflagrate when heated is not peculiar to graphite, but is shared by some forms of amorphous carbon. The authors consider that the term *carbon hydroxide* is preferable to such terms as graphitic acid or graphitic oxide. C. H. B.

Allotropic Silver. By A. J. A. PRANGE (*Rec. Trav. Chim.*, **9**, 121—133).—With the object of ascertaining the existence of argentous compounds, the author has examined the solutions of silver, and the silver dissolved therein, as described by Carey Lea (Abstr., 1890, 210), and confirms this observer's results.

The red solution is obtained by treating with water the blue-black precipitate formed by the interaction of dilute solutions of ferrous sulphate, sodium citrate, and of silver nitrate. This solution deposits a black powder in a few days, but when more dilute, remains free from precipitate for many weeks. In either case, when freshly prepared, the solutions are perfectly transparent to both incident and reflected light, whilst an intense ray of light passed through the solution undergoes no polarisation, thus proving the absence of suspended matter. Exposure to diffused light or to solar light causes decolorisation and precipitation of a black substance, and a similar effect is brought about by the addition to the solution of acids, alkalis, and neutral salts. As finely-powdered quartz or graphite also effects the precipitation, the author supposed a colloïdal silver to be present, and on dialysis of the solution no silver passed the membrane, but a deposit was thrown down thereon.

Alternate freezing and thawing of the liquid causes decolorisation and formation of a precipitate. The solution has very great absorptive power; a layer 1 c.c. thick, containing 0·7 gram silver per litre, allows no light to pass through.

A solution containing 4·75 grams silver per litre was of a syrupy consistence, the colour of bromine, very unstable, and contained much iron salt associated with the dissolved silver. The heat of dissolution for 1 gram Ag in 2·179 litres of water $= +250·8$ cal., and for 1 gram Ag in 0·2258 litre of water $= +126·73$ cal.

From the solution, the silver was obtained by adding ammonium nitrate, and, after the blue-black precipitate thus obtained had been well washed with water, containing sufficient ammonium nitrate to prevent redissolution, until the traces of iron salts were removed as far as possible, it was treated with alcohol, to remove adhering ammonium nitrate, and dried over sulphuric acid for several days; all these operations must be carried out in darkness, or Carey Lea's golden modification (*loc. cit.*) is obtained, instead of a heavy, deep, blue-black substance, which, on compression, assumes a metallic lustre and is easily powdered. This is quite insoluble in water, but dilute mineral acids and acetic acid dissolve it readily. When spread in the moist condition on glass or paper and dried, a beautiful mirror is obtained.

Careful analysis proved it to be free from combined oxygen, but traces of iron are a constant impurity. The heat of transformation to ordinary silver was calculated as $+60$ cal. per gram.

T. G. N.

Ternary Alloys. By C. R. A. Wright and C. Thompson (*Proc. Roy. Soc.*, **48**, 25—45).—The authors in this paper give an account of their experiments with mixtures of lead, zinc, and tin at high temperatures, and with mixtures of lead, zinc, and silver. Their general conclusions are as follows:—

A mixture of three metals, A, B, and C, of which A and B are each miscible in all proportions with C, but not with each other, will in general, when allowed to remain molten for a sufficient length of time at constant temperature, divide into two ternary alloys of unequal density, if the proportion of C present falls below a certain amount; but if the quantity of C present is above this limit, no separation takes place, and a homogeneous alloy results.

Under ordinary circumstances, the different alloys thus formed are respectively a saturated solution of A in a mixture of B and C, and one of B in a mixture of A and C, the solubilities being such that the greater the proportion of C present, the more of A (or B) is dissolved. Certain metals, however, appear to be capable of forming compounds in atomic proportions (for example, $AgZn_5$ and Ag_4Zn_5), in which case the quantity of A (or B) dissolved does not always vary directly with the amount of C present. The effect of temperature on different mixtures is very variable, but usually a rise of temperature increases the solubility of A in BC, and of B in AC, in some cases to a very considerable extent. The manner in which C divides itself between the two alloys depends on the nature and proportions of the metals present.

The numerical results are presented in numerous tables and curves.

J. W.

So-called Ammoniacal Mercury Compounds. By L. Pesci (*Gazzetta*, **20**, 485—504; compare Abstr., 1889, 347; 1890, 1211).—Rammelsberg and Kane have shown that a number of the complex compounds of mercury and ammonia may be regarded as containing the radicle $(Hg_2N)'$, *mercurammonium*. The author has also found (Abstr., 1890, 1211) that compounds containing this group are decomposed by the haloïd ammonium salts, and has described a method of quantitatively determining the "mercurammoniacal" nitrogen in compounds containing the radicle. It consists in placing under a bell-jar a mixture of the compound with a saturated aqueous solution of ammonium bromide coloured by litmus, and a vessel containing a known quantity of normal oxalic acid. The whole is left until the bromide solution acquires a clear purple colour. One fourth of the nitrogen in the ammonia absorbed by the acid is derived from the mercurammonium group in the compound, the reaction proceeding according to one of the following equations:—

I. $Hg_2NX + 3NH_4X = 2HgX_2 + 4NH_3$.
II. $Hg_2NR' + 4NH_4X = 2HgX_2 + NH_4R' + 4NH_3$.
III. $(Hg_2N)_2R'' + 8NH_4X = 4HgX_2 + (NH_4)_2R'' + 8NH_3$ (X = Cl, Br, I; $R' = NO_3$, BrO_3, &c.; $R'' = SO_4$, CO_3, &c.).

This method has been applied by the author to the elucidation of the constitution of the compound nitrates, sulphates, and iodides of mercury and ammonia, with the following results.

(1). *Nitrates.*—Six compounds are described by Gmelin, namely:—

a. $NH_2(Hg_3O_2)NO_3$; *b.* $NH_2(Hg_2O)NO_3$;
c. $NH_2(Hg_2O)NO_3,NH_2HgNO_3$; *d.* $2[NHg(Hg_3O_2)NO_3],Hg(NO_3)_2$;
e. $2NH_3,2Hg(NO_3)_2$; *f.* $NH_2(Hg_2O)NO_3,2NH_4NO_3,H_2O$.

a was prepared by Pagenstecher by supersaturating a solution of mercuric nitrate with ammonia, filtering, and allowing to evaporate; the author confirms Meyer's observation, that under these conditions the compound *e* only is formed. *b* was prepared by Kane and Soubeiron by precipitating a dilute solution of mercuric nitrate with a slight excess of ammonia, and washing the precipitate with boiling water. The author's analyses show that this compound is nothing but mercurammonium nitrate, $(Hg_2N)NO_3$. *c*, prepared by precipitating a neutral solution of mercuric nitrate with the necessary quantity of dilute ammonia, has the composition

$$(3Hg_2N)NO_3,NH_4NO_3 + 2H_2O.$$

It evolves ammonia when heated with caustic potash (contrary to Kane's statement), and it is converted into mercurammonium nitrate by the action of boiling water. *d* was prepared by Hirzel, by digesting yellow oxide of mercury with a moderately concentrated solution of ammonium nitrate. By following Hirzel's directions, the author was only able to obtain mercurammonium nitrate. *e*, obtained as described under *a*, has the constitution $(Hg_2N)NO_3,NH_4NO_3,H_2O$. On treatment with boiling water, it loses ammonium nitrate and is converted into mercurammonium nitrate. *f*, prepared by Kane by dissolving *c* in a boiling 20 per cent. solution of ammonium nitrate and filtering, has the constitution $(Hg_2N)NO_3,2NH_4NO_3,2H_2O$. It loses 1 mol. H_2O at 110—115°. It is decomposed by boiling water into mercurammonium nitrate and ammonium nitrate.

g. $(Hg_2N)NO_3,3NH_4NO_3$.—This is a new compound which is formed when a boiling 50 per cent. solution of ammonium nitrate is used in the preparation of the preceding compound. It may also be prepared by treating a concentrated solution of the basic nitrate, $Hg_2O(NO_3)_2$, with a 50 per cent. solution of ammonium nitrate. It crystallises in colourless, transparent needles which become almost opaque after exposure to the air for some time. Cold water abstracts ammonium nitrate from it, leaving the compound *c*; boiling water converts it into mercurammonium nitrate. It dissolves in ammonia, and on slowly evaporating the solution the compound *e* crystallises out in octahedra.

Sulphates.—Gmelin describes the compounds—

h. $2NH_3,3HgO,SO_3$; *i*. $2NH_3,2HgO,SO_3$;
j. $2NH_3,HgO,SO_3$; *k*. $2NH_3,HgO,SO_3H_2O$;
l. $3[(NH_2,Hg_2O)_2SO_4],NH_2HgSO_4$; *m*. $NH_2(Hg_3O_2),NH_2Hg_2O,SO_4$.

h, *i*, and *j* were prepared by Millon by saturating 100, 70, and 40 c.c. respectively of concentrated ammonia with mercuric sulphate, allowing the solution to evaporate over quicklime in an atmosphere of gaseous ammonia, and collecting the first crop of crystals in the first two cases, but evaporating to dryness to obtain the compound *j*. The author finds that whether 100 or 70 c.c. of ammonia are used, the first crop of crystals consist of octahedra having the composition $(Hg_2N)_2SO_4,2H_2O$; the crystals subsequently deposited have no constant composition. The product *j* is obtained in the manner described, but it is doubtful whether it is not a mixture of several substances. *k*, prepared by Schmieder by saturating a cold 20 per cent. solution of ammonium sulphate with yellow oxide of mercury and evaporating, has the composition $(Hg_2N)_2SO_4,3(NH_4)_2SO_4,4H_2O$. It is converted by cold water into the compound *l*, and by boiling water ultimately into mercurammonium sulphate. *l* is obtained by treating the preceding compound with cold water. It has the composition $7(Hg_2N)_2SO_4,(NH_4)_2SO_4,12H_2O$. It loses the whole of its water at 115°. *m* was obtained by Schmieder by dissolving *k* in dilute sulphuric acid and precipitating the solution with potash, but under these conditions the author could only obtain mercurammonium sulphate.

n. $5(Hg_2N)_2SO_4,14(NH_4)_2SO_4,16H_2O$.—This compound is formed when a mixture of a saturated solution of mercuric sulphate in ammonia (sp. gr. = 0·906) with an equal volume of a solution of ammonia saturated at 0° is allowed to remain for 24 hours. It crystallises in rectangular prisms which become opaque on drying in the air. It is converted by cold water into the compound *l*. It is readily soluble in ammonia, and the solution, when exposed to the air in presence of sulphuric acid, deposits crystals of mercurammonium sulphate.

Iodides.—Besides the compound $NH_2(Hg_2O)I$, shown by Rammelsberg to be the hydrate of mercurammonium iodide, namely, Hg_2NI,H_2O, Gmelin describes the compounds *o*, NH_3HgI_2, and *p*, $2NH_3HgI_2$. The former is considered by Rammelsberg to have the composition $Hg(NH_3I)_2 + HgI_2$, but the author's results lead to the formula $3Hg_2NI,4HgI_2,8NH_4I$; *p* is regarded by Rammelsberg as $Hg(NH_3I)_2$; the author finds, however, that it is formed when ammonia is added to a solution of mercuric iodide in ammonium iodide, and this renders it probable that its composition may be represented by the formula $Hg_2NI,3NH_4I$, since ammonia precipitates "fusible white precipitate," $Hg_2NCl,3NH_4Cl$, from solutions of mercuric chloride in ammonium chloride, and the compound $Hg_2NBr,3NH_4Br$ from solutions of mercuric bromide in ammonium bromide (Abstr., 1890, 1211).

S. B. A. A.

Manganese Oxides. By A. GORGEU (*Bull. Soc. Chim.* [3], **4**, 16—30; compare Abstr., 1889, 829; 1890, 260).—The author has prepared and examined specimens of hydrated manganese dioxide by all the known methods, and gives analytical data respecting the several products. The best yield is obtained by the action of dilute solutions of manganese nitrate and potassium permanganate on each other in presence of some free nitric acid.

As crystals of manganese nitrate when heated melt in their water of crystallisation, and then decompose at 125—145° to form manganese manganites, and at 150—165° to form manganese dioxide, the following method may be used for the production of anhydrous manganese dioxide:—600 to 800 grams of manganese nitrate crystals are warmed in a flask until red fumes appear, when the flask is to be removed from the flame, and the clear liquid decanted from the manganese manganites, and maintained at 150—160° for 40—60 hours, when a black, crystalline precipitate containing 99—100 per cent. of manganese dioxide is obtained, which is identical with polianite.

The several hydrated manganese dioxides differ in the amount of water of hydration they contain, according to the reactions by which they are formed, and to the experimental conditions, and it appears impossible to prepare a hydrated oxide by the wet method which shall correspond with an oxide of the formula MnO_2, on account of the tendency existing in this substance to combine with manganous oxide at the moment of liberation.

The hydrated oxides prepared below 105° redden litmus, neutralise definite quantities of solutions of the alkaline hydroxides, and give a brown solution in water which is transparent to direct light, whereas those prepared above 120°, together with the anhydrous dioxides and the minerals pyrolusite and polianite, do not; but even the last mentioned combine with hydrated manganous oxides to form manganese manganites, when left in contact under water for some days, and the reaction is accelerated by heat.

The hydrated oxides combine more readily with manganous oxide, the rate of action varying directly with their amount of water of hydration.

Both hydrated and anhydrous manganese dioxides evolve oxygen at 400°.

When hydrated manganese dioxide, prepared as above described, is left for some time in contact with very dilute solutions of metallic salts, corresponding manganites are formed, the cobalt and copper manganites corresponding with lanpadite and asbolite respectively.

Potassium permanganate is rapidly reduced to manganate by boiling a solution of the salt containing 20 per cent. of potassium hydroxide with an equivalent quantity of potassium manganite, produced by the action of carbonic anhydride on an alkaline solution of potassium permanganate. T. G. N.

Violet Chromium Fluoride. By G. FABRIS (*Gazzetta*, **20**, 582—584).—When violet chromium sulphate is heated with an excess of normal ammonium fluoride, the green, crystalline precipitate formed has the composition $CrF_3,3NH_4F$. When the reaction is allowed to proceed in the cold, the hydrated fluoride, $CrF_3 + 9H_2O$, is obtained. This compound is best prepared by adding the ammonium fluoride gradually to a cold solution of the chromium sulphate. It is insoluble in alcohol and in ammonium fluoride, and only very sparingly soluble in water; it dissolves in hydrochloric acid and in potash, forming violet and green solutions respectively. When heated in the air it loses its water, turns green, and is ultimately converted into chromium sesquioxide. S. B. A. A.

Artificial Production of a Chromium Blue. By J. GARNIER (*Compt. rend.*, **111**, 791).—Potassium chromate, 48·62 parts, calcium fluoride, 65 parts, and silica, 157 parts, are fused in a brasqued crucible. A blue glass is obtained, surrounded by a pellicle of metallic chromium. C. H. B.

Action of Ammonia on Solutions of Normal Ammonium Titanofluoride. By A. PICCINI (*Chem. Centr.*, 1890, ii, 544; *Rend. Acad. Lincei*, **6**, i, 568—571).—If an excess of ammonia is added to a solution of ammonium titanofluoride, $TiF_4.2NH_4F$, the whole of the titanic acid is precipitated. If, however, ammonia is added drop by drop to the warm solution of the fluoride, the white precipitate which first forms redissolves later, until at a certain point the liquid has merely an opalescent appearance: if now allowed to remain, a white, crystalline precipitate settles out. It is completely soluble in a solution of ammonium titanofluoride, but is decomposed by water, titanic acid being precipitated. The author ascribes to it the formula $3(TiF_4,2NH_4F),2TiO_2,3NH_4F$. J. W. L.

Atomic Weight of Bismuth. By R. SCHNEIDER (*J. pr. Chem.* [2], **42**, 553—565).—In this paper, the author criticises Classen's memoir on this subject (Abstr., 1890, 706). He complains that the consideration of Marignac's work is dismissed too summarily by

Classen, and that the criticisms thereon are not valid. The accusation against the bismuth which the author and Marignac used, of containing lead, is trivial; for even if it contained as much as 0·25 per cent. of lead, which is practically impossible, the atomic weight would only be raised 0·17, an amount which is well within the limits of variation in the determinations. The author criticises Classen's apparatus and concludes that his atomic weight, 208·9 ($O = 16$), is less likely to be correct than 208·07. A. G. B.

Action of Hydrogen Sulphide on certain Metallamines. By E. F. SMITH and H. F. KELLER (*Ber.*, **23**, 3373—3375).—On passing pure hydrogen sulphide over palladio-ammonium chloride at 70—80°, the salt becomes black, and at higher temperatures ammonium chloride volatilises; the residue is insoluble in any one acid, but dissolves sparingly in aqua regia, and probably has the formula PdS. Purpureocobalt chloride, roseocobalt sulphate, and luteocobalt chloride react in a similar manner with hydrogen sulphide at ordinary temperatures, whilst purpureochromium chloride requires to be heated almost to the dissociation temperature of hydrogen sulphide before any change occurs. J. B. T.

Mineralogical Chemistry.

Celestine containing Free Sulphur. By H. J. JOHNSTON-LAVIS (*Min. Mag.*, **8**, 28—29).—The author describes some crystals of celestine from Girgenti, Sicily, containing as much as 13·69 per cent. of sulphur. The sp. gr. of the crystals was 3·739, the included sulphur lowering the sp. gr. of its host. It would appear that part of the sulphur crystals and celestine formed simultaneously, and the latter was compelled to include the sulphur grains as its crystals grew in size. B. H. B.

Elaterite from Ross-shire. By W. MORRISON (*Min. Mag.*, **8**, 133—134).—This mineral tar is an intensely black, lustrous, sticky substance found in fissures in the conglomerate above the old red sandstone at the Craig Well, near Dingwall. On dry distillation, it yields an inflammable oil, gas, and water. It melts at 140°, leaving on ignition a slight ash containing ferric oxide and lime. B. H. B.

Analyses of various Minerals. By I. MACADAM (*Min. Mag.*, **8**, 135—137).—The author gives the results of analyses of diatomite from Mull, of bornite and malachite from the limestone of Kishorn, Ross-shire, of galena and zinc-blende from Tyndrum, Perthshire, of fichtelite from Handforth, Cheshire, and from Shielding, in Ross-shire, and lastly of elaterite from Dingwall. The last, described in the preceding abstract, gave the following results :—

C.	H.	O, &c.	N.	S.	Total.
81·19	13·37	4·45	0·13	0·86	100·00

B. H. B.

Identity of Bruiachite and Fluorspar. By M. F. HEDDLE (*Min. Mag.*, **8**, 274—277).—The mineral from Loch Bhruithaich, in Inverness-shire, described in 1887, under the name of *bruiachite* (*Min. Mag.*, **7**, 42), is found by the author to be fluorspar, the analysis giving the following results :—

Ca.	F.	$BaSO_4$.	Total.
51·12	48·56	0·23	99·91

B. H. B.

Pyrargyrite and Proustite. By H. A. MIERS (*Min. Mag.*, **8**, 37—102).—This is an exhaustive monograph on the red silver ores. The literature is collated, and the crystalline forms previously observed are tabulated. Excluding a number of doubtful forms, the author has determined 23 new forms on pyrargyrite crystals, and four new forms on proustite crystals. The results are given of 15 analyses of specimens in the British Museum. The variations in the rhombohedron angle among the whole series of pyrargyrite analysed fall within the irregular variations in individual specimens, and cannot be ascribed to the presence of varying quantities of arsenic. The same is true of proustite containing antimony. (Compare Abstr., 1888, 657.) B. H. B.

Crystals of Copper Pyrites. By S. L. PENFIELD (*Amer. J. Sci.*, **40**, 207—211).—The author gives a crystallographical description of some very unusual and interesting crystals of copper pyrites from the French Creek iron mines, Chester Co., Pennsylvania, the locality from which some curiously developed crystals of iron pyrites have been obtained. It is very remarkable that at this one locality crystals of iron pyrites are found imitating tetragonal and orthorhombic symmetry, and crystals of copper pyrites imitating isometric and hexagonal rhombohedral symmetry. B. H. B.

Metacinnabarite from California. By W. H. MELVILLE (*Amer. J. Sci.*, **40**, 291—295).—An excellent specimen of metacinnabarite found in the quicksilver mine of New Almaden, California, gave on analysis the following results :—

S.	Hg.	Fe.	Zn.	Mn.	$CaCO_3$.	Quartz.	Org. matter.
13·68	78·01	0·61	0·90	0·15	0·71	4·57	0·63

The mineral occurs in finely developed and brilliant crystals belonging to the rhombohedral system. The sp. gr. is 7·118. The crystals exhibit a high metallic lustre and black colour. They are brittle with a hardness of 2. (Compare Penfield on metacinnabarite crystals from California, Abstr., 1886, 314.) B. H. B.

Mangano-magnesian Magnetite. By A. H. Chester (*Min. Mag.*, **8**, 125—126).—A mineral from New Zealand was analysed with the following results:—

Fe_2O_3.	FeO.	Mn_3O_4.	MgO.	CaO.	SiO_2.	Total.
66·71	19·62	4·63	7·15	trace	2·38	100·49

From these figures, it is seen to be a magnetite, in which part of the ferric oxide is replaced by manganic oxide, and part of the ferrous oxide by manganous oxide and magnesium oxide. It may, therefore, be called a mangano-magnesian magnetite, a variety not noticed hitherto. B. H. B.

Dufrenite from Cornwall. By E. Kinch (*Min. Mag.*, **8**, 112—115).—The mean of a number of analyses of botryoidal dufrenite from Wheal Phœnix gave the following results:—

H_2O.	SiO_2.	P_2O_5.	FeO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Total.
11·47	0·43	31·10	6·80	47·03	0·87	1·68	0·17	99·55

From these results, there seems no reason to doubt that pure specimens of dufrenite contain a higher ratio of acid to base than that indicated by the formula usually ascribed to the species,

$$2Fe_2O_3,P_2O_5,3H_2O.$$

The formula suggested by the author is $3Fe_2O_3,FeO,2P_2O_5,6H_2O$.
B. H. B.

Ferric Sulphates from Chili. By F. A. Genth and S. L. Penfield (*Amer. J. Sci.*, **40**, 199—207).—The authors describe some excellent specimens of the ferric sulphates from the Mina de la Compania, near Sierra Gorda, in the Province of Tocapilla.

1. *Amarantite* (Abstr., 1888, 923).—The crystallisation is triclinic; colour brownish-red; hardness 2·5; sp. gr. 2·286. Analysis (No. I) gave the formula $Fe_2S_2O_9 + 7H_2O$. [Compare analyses by Frenzel, Abstr., 1888, 923; Mackintosh, Abstr., 1890, 454; and Darapsky, Abstr., 1890, 456.]

2. *Sideronatrite.*—Optical properties indicate orthorhombic symmetry. Hardness 1·5; sp. gr. 2·355. Analysis (No. II) gives the formula $2Na_2SO_4,Fe_2S_2O_9 + 7H_2O$.

3. *Ferronatrite* (Abstr., 1890, 455).—No distinct crystals were observed, but the cleavage and the optical properties show that the crystallisation must be hexagonal. Hardness 2·5; sp. gr. 2·547. Analysis (No. III) gave results agreeing with the formula

$$3Na_2SO_4,Fe_2S_3O_{12} + 6H_2O.$$

	H_2O.	SO_3.	Fe_2O_3.	CaO.	Na_2O.	K_2O.
I.	28·29	35·46	37·46	trace	0·59	0·11
II.	17·07	44·22	21·77	—	16·39	—
III.	11·89	51·30	17·30	0·22	19·95	0·16

4. *Utahite.*—Minute, brownish-white scales from the Mimbres mine,

Georgetown, New Mexico, gave, on analysis, results corresponding with the formula Fe_2SO_6.

5. The authors have also examined some perfect crystals of *atacamite*, brought with the ferric sulphates from the Sierra Gorda. The analysis gave results agreeing with the formula $CuCl_2,3Cu(OH)_2$.

B. H. B.

Contributions to Mineralogy. By F. A. GENTH (*Amer. J. Sci.*, **40**, 204—207).—*Picropharmacolite*, from Joplin, Missouri, occurring in incrustations of dolomite, appears to be a mixture of several varieties of the same mineral. Analysis gave the following results :—

	H_2O.	CaO.	MgO.	MnO_2.	As_2O_5.
I.	23·11	22·42	6·64	0·26	47·60
II.	24·58	19·64	8·41	0·29	47·74
III.	20·35	17·09	11·54	0·31	50·56

I. Botryoidal crusts, made up of radiating fibres, sp. gr. 2·583. Formula $(H_2CaMg)_3As_2O_8 + 6H_2O$. II. Crusts mixed with globular aggregations. III. Radiating silky groups, after the powder had been placed over sulphuric acid for a month.

Pitticite, from the Clarissa mine, Tintic District, Utah, occurring in cryptocrystalline masses, gave results corresponding with the formula $4(Fe_2As_2O_8),Fe_2(OH)_6 + 20H_2O$.

The so-called *gibbsite* from Chester Co., Pennsylvania, is found by the author to be a hydrous aluminium phosphate of unknown constitution.

B. H. B.

Dudgeonite, Hydroplumbite, and Plumbonacrite. By M. F. HEDDLE (*Min. Mag.*, **8**, 200—203).—*Dudgeonite* is the name given by the author, after its discoverer, to a mineral found in the Pibble mine, Kirkcudbrightshire. It occurs in cavities in copper-nickel. It is a greyish-white solid, having a hardness of 3 to 3·5, and giving, on analysis, the following results :—

NiO.	CoO.	CaO.	As_2O_5.	H_2O.	Total.
25·01	0·76	9·32	39·33	25·01	99·43

Its formula is $(\frac{2}{3}NiO + \frac{1}{3}CaO)_3As_2O_5 + 8H_2O$, that of annabergite with one-third of the nickel oxide replaced by lime.

A mineral partially described by the author is thought to have come from Leadhills, and to have the formula $3PbO,H_2O$. The crystals are white, and probably hexagonal. The name proposed is *hydroplumbite*.

A mineral from Leadhills, which appeared to be hydroplumbite, gave, on analysis, results corresponding with the formula $PbCO_3,3PbO,H_2O$. Not being a hydrated cerrusite, it may be called *plumbonacrite*.

B. H. B.

Silicate containing Copper and Silver. By E. JACQUEMIN (*Bull. Soc. Chim.* [3], **4**, 255).—A mineral, called "pierre verte," obtained from a lode near Bussang, contained silver, corresponding with 210—225 grams per tonne, and copper equal to 35—45 kilos. per tonne, and appears to be a copper hydrosilicate accompanied by a cupro-argentic silicate and cupric ferric silicate in a siliceous matrix.

T. G. N.

Minerals from the Lizard. By J. J. H. TEALL (*Min. Mag.*, **8**, 116—120).—The author gives the following analytical results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	Ignition.
I.	49·9	6·2	1·7	0·6	3·9	0·4	20·4	16·1	—	—	0·9
II.	49·4	29·8	1·2	—	—	—	12·6	1·7	3·3	0·4	1·7
III.	48·8	10·6	1·7	trace	4·7	—	12·2	18·6	—	—	1·8
IV.	52·8	2·8	1·8	—	—	—	25·2	16·1	—	—	0·5
V.	50·8	3·6	3·7	trace	6·8	—	1·2	26·1	0·2	—	5·8

I. *Chrome-diopside*, found as a constituent of gabbro at Coverak, Cornwall. The mineral has a sp. gr. of 3·2. II. *Labradorite*, associated with the chrome-diopside and olivine in the gabbro mentioned above. III. *Hornblende*, a very pale-coloured variety, occurring in a gabbro schist at Pen Voose. IV. *Malacolite*, occurring with labradorite, sphene, and an unknown mineral as constituents of an extremely hard and finely crystalline rock at Karakclews. Much of the so-called saussurite of the Lizard is similar to this rock in composition. V. *Anthophyllite*, occurring in a zone surrounding the altered olivine in some varieties of the Lizard gabbros. It is evidently a secondary mineral resulting from the alteration of olivine.

B. H. B.

Mordenite. By L. V. PIRSSON (*Amer. J. Sci.*, **40**, 232—237).—Under the name of mordenite, How published (Trans., 1864, 100) a description of a new zeolite occurring at Morden Point, Nova Scotia. To this species he assigned the formula $RO,R_2O_3(SiO_2)_9,6H_2O$. The accuracy of this formula has been questioned, but the author announces the re-discovery of this interesting mineral from the Hoodoo Mountain, in Western Wyoming, and proves the accuracy of How's work. The analytical results obtained were as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
66·40	11·17	0·57	1·94	0·17	3·58	2·27	13·31	99·41

These results are closely in accord with How's formula. Under the name of ptilolite, Cross and Eakins (Abstr., 1886, 990) described a new zeolite with a formula strikingly similar to that of mordenite. In the crystal form and optical properties, however, the two zeolites are entirely unlike.

B. H. B.

Large Porphyritic Crystals of Felspar. By T. H. HOLLAND (*Min. Mag.*, **8**, 154—157).—In consequence of the striking analogies which have been shown to exist between the basalts of Iceland and those of Mull, the author has undertaken an examination of the porphyritic felspars occurring in the lavas of Mull. The crystals examined are an inch or more across, yellowish-green in colour, and have a sp. gr. of 2·72. On analysis, they yielded—

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	Na_2O.	Ignition.	Total.
50·80	31·54	12·83	3·96	0·52	99·65

These results are in close agreement with those obtained by other observers with the Icelandic felspars. B. H. B.

Conversion of a Felspar into a Scapolite. By J. W. JUDD (*Min. Mag.*, **8**, 186—198).—At Bamle, in Norway, observations prove that a pyroxene-felspar rock has been converted into a hornblende-scapolite rock. A microscopic study of this rock, described in great detail by the author, proves that the scapolite has been produced by a plagioclase felspar, and that in most cases the change is incomplete. After the felspar crystals had become charged along their solution planes with cavities containing sodium chloride, the effect of internal stresses in the rock-mass was to bring about those chemical reactions by which the felspar molecules were broken up, and their material became united with the sodium chloride to form scapolite.

B. H. B.

Occurrence of Silver in Volcanic Dust. By J. W. MALLET (*Proc. Roy. Soc.*, **47**, 277—281).—The author had already detected silver in the volcanic ash from Cotopaxi (Abstr., 1877, 454). He has now found a trace of the same metal in the dust obtained during the eruption of Tunguragua (Ecuador) on the 11th January, 1886. The mountain had been quiescent for over a century. Besides the chief constituents, silica and alumina, the ash contains considerable quantities of the oxides of iron, calcium, and sodium, together with smaller quantities of the carbonates of calcium and magnesium. The silver amounts to one part in 107,200, and is probably present as chloride; for, though easily dissolved by solution of potassium cyanide or thiosulphate, it is not extracted by nitric acid. The Cotopaxi ash contained one part of silver in 83,600. J. W.

Two New Iron Meteorites. By E. E. HOWELL (*Amer. J. Sci.*, **40**, 223—226).—1. *Meteorite from Hamilton Co., Texas.*—This was discovered in 1887. It weighed 179 lbs., the two greater dimensions being $17\frac{1}{2}$ and 13 inches. The Widmanstätten figures are brought out with remarkable rapidity on the application of very dilute acid. The amount of troilite found in cutting the iron is not great, and seems to be distributed in thin, narrow plates, no nodules having been met with. On analysis, the iron yielded the following results :—

Fe.	Ni.	Co.	Cu.	P.	S.	C.	Total.
86·54	12·77	0·63	0·02	0·16	0·03	0·11	100 26

Its sp. gr. is 7·95.

2. *Meteorite from Puquios, Chili.*—This is said to have been found in 1884. It weighed 14 lbs. $7\frac{1}{2}$ ozs., the two largest diameters being 10 and $5\frac{1}{2}$ inches. The surface of the iron is unusually smooth, only a few shallow pittings being visible. The etched sections show that the mass has been subjected to fracture and dislocation, result-

ing in an undoubted faulting of the Widmanstätten figures and of the troilite. In all probability these are the first faults observed in an iron meteorite. They are clearly not produced by the impact of the fall upon the earth, but are a part of the meteorite's earlier history. On analysis, the iron yielded the following results:—

Fe.	Ni.	Co.	Cu.	P.	S.	C.	Total.
88·67	9·83	0·71	0·04	0·17	0·09	0·04	99·55

Its sp. gr. is 7·93. B. H. B.

Five New American Meteorites. By G. F. Kunz (*Amer. J. Sci.*, **40**, 312—323).—1. *Meteorites from Brenham Township, Kiowa Co., Kansas.*—20 meteorites, weighing altogether 2000 lbs., were found in this district in 1886. The following is an analysis of these meteorites:—

Fe.	Ni.	Co.	Cu.	P.	S.	C.	Si.
88·49	10·35	0·57	0·03	0·14	0·08	trace	trace

The olivine (I) and the dark outer zone of olivine (II) gave the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	NiO.	CoO.	MnO.	MgO.	S.
I.	40·70	trace	0·18	10·79	0·02	—	0·14	48·02	—
II.	34·14	—	—	23·20	trace	0·03	0·09	40·19	5·42

The sp. gr. of the iron freed from olivine was 7·93, whilst that of the olivine was 3·376. The iron is brilliant white, enclosing the troilite, and surrounding the olivine crystals. The outer zone of dark-brown olivine is in reality composed of an intimate mixture of troilite and olivine. This group of meteorites is of special interest, because of the probable connection with the meteoric iron found in 1883 in the Turner mounds in Ohio.

2. *Meteorite from Winnebago Co., Iowa.*—This meteorite was observed to fall on May 2nd, 1890. It is a typical chondrite, with a sp. gr. of 3·638, and is composed approximately of 19·40 per cent. of nickeliferous iron, 6·19 per cent. of troilite, 36·04 per cent. of silicates soluble in hydrochloric acid, and 38·37 per cent. of silicates insoluble in hydrochloric acid. The nickeliferous iron on analysis gave the following results:—

Fe.	Ni.	Co.	P.	Total.
92·65	6·11	0·65	trace	99·41

3. *Meteoric Stone from Ferguson, Haywood Co., North Carolina.*—This fell on July 18, 1889. Its weight was about 8 ozs., and it very closely resembled the meteoric stone from Mocs, Transylvania.

4. *Meteoric Iron from Bridgewater, Burke Co., North Carolina.*—This weighs 30 lbs., and measures 22½ by 15 by 10 cm. It belongs to the caillite group, and resembles the Cabin Creek and Glorietta Mountain meteorites in structure. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Cl.	Total.
88·90	9·94	0·76	0·35	0·02	99·97

Its sp. gr. was 6·617.

5. *Meteoric Iron from Summit, Blount Co., Alabama.*—This meteorite weighs 2·2 lbs., and measures 5 by 2 by 3 inches. It contains a large quantity of free iron chloride, and showed only a slight trace of the original crust, being almost completely oxidised. On etching with nitric acid, no Widmanstätten figures were developed, but merely a fine marking similar to that of the Linnville meteorite. Analysis gave the following results:—

Fe.	Ni.	Co.	P.	Total.
93·39	5·62	0·58	0·31	99·90

The sp. gr. was found to be 6·949. B. H. B.

Australian Meteorites. By A. LIVERSIDGE (*Chem. News*, **62**, 267).—The *Thunda meteorite*, found near Windorali, in the Diamantina District, Queensland, weighed 137 lbs., had a sp. gr. 7·78, and a well-marked crystalline structure; it was also remarkable for numerous nodules of iron sulphide, which in crystallising seem to have given rise to the numerous fissures that proceed from them. It consists essentially of nickeliferous iron containing a trace of cobalt and a small quantity of sulphur, phosphorus, and carbon.

Various earthy meteorites have been found in New South Wales. Of the three *Barratta meteorites*, the first, which has already been described, has a sp. gr. 3·429; the second weighs 31 lbs., sp. gr. 3·706; the third weighs 48 lbs., sp. gr. 3·429; the *Gilgoin meteorite* weighs 67½ lbs., sp. gr. 3·857; the *Eli Elwah*, 33½ lbs., with a sp. gr. of 3·537. These consist essentially of magnesium silicates (as enstatite), with more or less nickeliferous iron and some other substances in small quantities; they resemble one another in character, showing some variation in being more or less cracked or granular.

D. A. L.

Mineral Water of Penon de los Banos, Mexico. By L. L'HÔTE (*J. Pharm.* [5], **22**, 427—430).—The spring occurs on the side of a hill of gravel about 4 kilom. north-east of Mexico. The water is perfectly limpid and inodorous. Its taste is first slightly acid, then alkaline; its temperature 44·5°. L. Rio de la Loza found the atmosphere at the spring to contain:—Air (?), 6·2; carbonic anhydride, 63·3; nitrogen, 28·8; water, 1·7 per cent. by volume. Sp. gr. of the water at 15° when received by the author, 1·00174. Total solid residue, 2·216 grams per litre. Arsenic, iodine, and bromine could not be detected. The solid residue contained:—

Sodium carbonate	0·1834	grams	per litre.
Potassium carbonate	0·2945	,,	,,
Calcium carbonate	0·4039	,,	,,
Magnesium carbonate	0·4286	,,	,,
Sodium sulphate	0·0074	,,	,,
,, phosphate	0·0013	,,	,,
,, borate	traces	,,	,,
,, chloride	0·7366	,,	,,
Lithium chloride	0·0060	,,	,,
Silica	0·1522	,,	,,
Alumina	0·0012	,,	,,
Iron oxide	0·0009	,,	,,
Organic matter	traces	,,	,,
	2·2160		

The water is closely analogous to those of Royat and Mont-Dore (Auvergne). J. T.

Hot Spring Waters. By A. Liversidge (*Chem. News*, **62**, 264—266).—Four samples of water from hot springs on Ferguson Island were examined. The surface rocks of this island are principally slatey, but the immediate neighbourhood of the hot springs has all the usual characters of such localities—incrustations, sulphur hillocks emitting sulphurous fumes and steam, seething mud pools, &c. Each of the four samples of water had a sediment consisting mostly of sulphur; in one sample (1) it was blue, and contained a few diatom frustules and small crystals of selenite, in another (4) it was brown, whilst in the others (2 and 3) it was yellow. Sample 1 reacted acid, had a strong odour of sulphurous anhydride, deposited sulphur on exposure to the air, and, on evaporation, left a pale-brownish, hygroscopic residue, which, on ignition, intumesced and gave off sulphuric fumes, leaving a mass, yellow when hot and brown when cold, consisting of soluble and insoluble silica, iron (originally ferrous), magnesia, lime, and sodium chloride in abundance. The other samples were very similar: sample 2 contained a good deal of free sulphuric acid and lithium, whilst samples 3 and 4 contained both sulphurous acid and hydrogen sulphide, and also lithium. These samples gave, in parts per 1000, the numbers under 1, 2, 3, 4 in the following table:—

	1.	2.	3.	4.	5.
Total solids	14·10	4·90	3·10	7·58	0·76
Loss on ignition	9·63	1·27	0·63	2·11	0·34
Chlorine	—	1·24	0·73	1·39	—

Sample 5 is a water from a hot spring on Savo Island; it had a black deposit consisting of particles of iron sulphide, of quartz, and other transparent minerals with a few diatom frustules. The water was clear, slightly acid, highly charged with hydrogen sulphide, and on exposure deposited sulphur. The residue from its evaporation was whitish, sulphurous, and silky-looking, and on ignition gave off much steam, and blackened; the carbonaceous matter burnt away slowly. Hydrochloric and sulphuric acids, hydrogen sulphide, silica, iron, aluminium, calcium, magnesium, and sodium were detected.

A sample of water from a fresh water lake on the raised atoll known as Santa Anna was of the density of fresh water, tasted flat and fresh, rapidly decolorised permanganate, and contained, besides plenty of chlorides, some lime and ammonia. The lake is cut off from the sea by a swampy tract one-third of a mile across.

Some samples from the trachytic island of Simbo were examined. This island at the southern portions has indications of dying volcanic activity. At an elevation of 300 feet, there are fumeroles emitting steam, temperature 208—210° F., hydrogen sulphide, and sulphurous acid, and depositing sulphur, alum, sodium chloride, milky opal, iron stains, &c.; the water from them shows sulphurous acid and hydrogen sulphide, but no hydrochloric or carbonic acid. A fumerole at an elevation of 1100 feet above the sea discharged principally aqueous vapour at a temperature of 175—180° F., very slightly acid, but containing neither hydrogen sulphide nor hydrochloric acid, nor sulphurous or carbonic anhydride, and forming no deposit round the orifice. D. A. L.

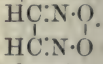
Organic Chemistry.

Active Amyl Derivatives. By P. A. GUYE (*Compt. rend.*, **111**, 745—747).—If the views previously explained (Abstr., 1890, 722) are correct, any substitution in the group CH_2Cl in active amyl chloride that keeps the mass of this group higher than that of the unaltered H, Me, and Et groups will yield derivatives with a rotatory power of the same sign as that of the amyl chloride. Examination of forty amyl derivatives, which may be regarded as derived from the active chloride in the way indicated, proved that this deduction is correct. C. H. B.

Hydrolysis of Halogen Carbon Compounds. By C. CHABRIÉ (*Compt. rend.*, **111**, 747—748).—Ethylene fluoride is obtained as a colourless gas by heating ethylene bromide at 200° with silver fluoride. It is absorbed by lime water, with formation of glycol and calcium fluoride. The author is endeavouring to obtain erythrol in a similar manner. He has also investigated the action of halogen derivatives on boric anhydride at a high temperature. Ethylene bromide and glycerol tribromhydrin yield a considerable quantity of boron bromide at 250°. Carbon tetrachloride yields boron chloride in large quantity; tetrachlorethylene reacts with less energy and hexachlorobenzene yields no boron chloride. Carbon tetrachloride, silver fluoride, and amorphous boron yield gases containing fluorine, chlorine, carbon, and boron, with some deposition of carbon and boron, and a small quantity of silver. C. H. B.

β-Dipropylene. By F. COUTURIER (*Bull. Soc. Chim.* [3], **4**, 30—31).—If pinacone, after treatment with sulphuric acid, is submitted to distillation, it yields, in addition to pinacoline, a liquid boiling at 60—70°, which on fractionation affords an impure substance boiling at 65°; this, when heated with calcium chloride in sealed tubes, and subsequently fractionated over sodium yields *β-dipropylene*, C_6H_{10}, which boils at 69·5°. It neither forms a compound with cuprous chloride nor with silver nitrate in ammoniacal solution, but yields a tetrabromide, $C_6H_{10}Br_4$, which is soluble in alcohol and in ether; it must, therefore, differ in constitution from the isomeric hydrocarbon, boiling at 39°, prepared by Favorsky (Abstr., 1888, 798) by the action of alcoholic potash on pinacoline dichloride, and probably has the constitution $CH_2{:}CMe{\cdot}CMe{:}CH_2$. By the action of acetic anhydride on pinacone at 80—90° for several days, a crystalline diacetyl derivative of pinacone and a small quantity of β-dipropylene are obtained; the yield of the diacetyl derivative is further enhanced if the action is maintained in the cold during several weeks, when it may be extracted by dissolving the excess of pinacone in water, and recrystallising the residual crystals from ether. T. G. N.

Constitution of Fulminic Acid. By R. SCHOLL (*Ber.*, **23**, 3505—3519).—Although the author's researches on this subject are not yet complete, he has thought it necessary, in view of the recent paper of Holleman (this vol., p. 64), to publish the results obtained up to the present time. From results obtained in his researches on the alkylated glyoxime peroxides, it appeared not impossible that fulminic acid might be glyoxime peroxide itself,



$\begin{array}{l}HC{:}N{\cdot}O\\ \ \ \vert\qquad\ \ \vert\\ HC{:}N{\cdot}O\end{array}$.

Against this supposition, however, is the fact that phenylglyoxime peroxide does not yield salts (see this vol., p. 316), and that ethereal salts cannot be prepared from mercuric fulminate. The author also finds that it cannot be converted into acid derivatives of phenylglyoxime peroxide, but that by the action of acetic chloride the chief product obtained is *acetylisocyanic acid*, CONAc. To carry out the last-named reaction, mercuric fulminate is mixed with light petroleum, and an excess of acetic chloride added. Hydrocyanic acid and a small quantity of isocyanic acid are evolved, and acetylisocyanic acid passes into solution. The latter has not yet been isolated, but that it has really the constitution assigned to it is shown by the facts that it unites with alcohol forming ethyl acetylcarbamate, $NHAc{\cdot}COOEt$, with ammonia to form monacetylcarbamide, $H_2N{\cdot}CO{\cdot}NHAc$, and with acetamide to form symmetrical diacetylcarbamide, $CO(NHAc)_2$. Further, it is resolved by water into carbonic anhydride and acetamide. The residue which remains after separating the light petroleum solution consists chiefly of mercuric chloride, but contains also small quantities of acetylcarbamide, and symmetrical diacetylcarbamide. The formation of the latter can be readily explained, as part of the acetylisocyanic acid is decomposed by traces of moisture with formation of acetamide, which then combines with unaltered acetylisocyanic acid, forming symmetrical diacetylcarbamide. The properties of this substance agree fully with the description of Schmidt (Abstr., 1872, 718), who does not, however, give its melting point, which the author finds to be 152—153°.

Attempts were made to isolate acetylisocyanic acid, by using nitrobenzene as diluent in the above reaction, and carefully fractionating the product under diminished pressure. A liquid was obtained boiling at 78—80°, which is not, however, pure acetylisocyanic acid, but appears to contain about 14 per cent. of acetonitrile. Somewhat similar results were obtained by Schützenberger (*Compt. rend.*, **54**, 154) in attempting to prepare this compound from acetic chloride and silver isocyanate.

The yield of acetylisocyanic acid actually obtained amounted to more than 50 per cent. of the theoretical, and it would therefore appear that this is the only primary reaction, and that the other products are all formed by secondary reactions. The formula which most readily explains this is Steiner's (Abstr., 1883, 1074), namely, $HO{\cdot}N{:}C{:}C{:}N{\cdot}OH$, but it is difficult to understand how a compound of this constitution, containing two carbon atoms united by double linkage, should be formed by the oxidation of alcohol.

H. G. C.

Action of certain Inorganic Salts on the Specific Rotatory Power of Cane-sugar. By K. FARNSTEINER (*Ber.*, **23**, 3570—3578).—In this paper, an account is given of the action of the chlorides of the metals of the alkalis and of the alkaline earths on the specific rotatory power of cane-sugar. The author finds that with a constant relation of sugar to water, the chlorides of strontium, barium, and magnesium cause a decrease in the rotation, which continues to diminish as the quantity of salt added is increased. The first action of chloride of calcium is to cause a decrease in the rotation, which, however, on the addition of a certain quantity of the salt, reaches a maximum, further addition causing an increase in the rotation, which eventually exceeds that of the pure sugar solution.

If the relation of sugar to the salt be kept constant, and the quantity of water varied, it is found that the addition of water causes in all cases an increase in the specific rotatory power, that is, the action of the salts is lessened. The specific rotatory power is almost unaffected by varying the quantity of sugar with a constant relation between salt and water. The chlorides of lithium, sodium, and potassium behave in a similar manner.

An examination of the action of the same quantities of different salts shows that in the case of strontium, calcium, and magnesium the depression varies inversely with the molecular weight, and that the product of the two quantities is approximately a constant. Barium chloride does not act in the same manner, but the chlorides of the alkalis show a similar relation. The relation, however, only holds within each group of chlorides, and not for two salts belonging to different groups.

H. G. C.

Starch. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **23**, 3473). —A reply to the recent communication of Zulkowsky (this vol., p. 165) on the same subject.

Gummy Exudation from the Sugar Beet. By E. O. v. LIPPMANN (*Ber.*, **23**, 3564—3566).—A number of large, unripe beet-roots, which had been allowed to remain for some weeks in paper, were found at the end of that time to show a very remarkable appearance. Without any particular bruising being visible, a number of resinous drops had separated out in the furrows which commonly occur in the root, and had flowed together forming a hard, brittle, tasteless, and odourless mass, which could be readily and completely separated from the roots. In appearance it resembled the ordinary plant gums; it was insoluble in cold water and alcohol, and on burning evolved the characteristic odour of the carbohydrates, leaving only a trace of ash. It slowly dissolved in boiling alkalis, and was precipitated from the neutralised solution by alcohol. When freshly precipitated, it dissolved in water, forming a neutral, dextrorotatory solution. On boiling with dilute sulphuric acid, furfuraldehyde distilled over, and arabinose and galactose were found in the residue; when oxidised with nitric acid, it yielded mucic acid. From these results, it would appear possible that the compound is an anhydride of arabinose and galactose, $C_5H_{10}O_5 + C_6H_{12}O_6 - H_2O = C_{11}H_{20}O_{11}$. The analysis of the crude compound agrees fairly closely with this formula, as also does the quantity of furfuramide and of mucic acid obtained in the foregoing reaction. The lack of material has, however, put an end to further investigation, as no other case of the formation of the gum-like compound has been observed, even when the roots have been specially bruised. H. G. C.

Diisobutylamine Ethyl Oxalate. By H. MALBOT (*Bull. Soc. Chim.* [3], **4**, 253).—When an alcoholic solution of oxalic acid is added to diisobutylamine, a white precipitate is formed, which consists of diisobutylamine hydrogen oxalate and of diisobutylamine ethyl oxalate, resulting from the action of the former substance on the alcohol; the mixture is crystallised from boiling alcohol, when the diisobutylamine hydrogen oxalate first separates as brilliant scales, and the mother liquor on evaporation yields acicular crystals of the ethyl salt, $COOEt{\cdot}COO{\cdot}NH_2(C_4H_9)_2$; these are dried over sulphuric acid, and are recrystallised from boiling ether. When the substance is heated with water in a reflux apparatus for several days, diisobutylamine hydrogen oxalate is produced. The author is continuing the study of the compound. T. G. N.

Action of Propaldehyde on Alcohols. By S. B. NEWBURY and M. W. BARNUM (*Amer. Chem. J.*, **12**, 519—520; compare Geuther, *Annalen*, **126**, 63).—*Propylidene diethyl ether*, $CH_2Me{\cdot}CH(OEt)_2$, is obtained by heating for 12 hours in a closed flask at 100° a mixture of propaldehyde (1 vol.), ethyl alcohol (2 vols.), and glacial acetic acid ($\frac{1}{2}$ vol.). The product is shaken with a strong solution of calcium chloride to remove unchanged alcohol, dried, and submitted to fractional distillation. The pure ether boils at 122·8° under a pressure of 744 mm., and has a specific gravity of 0·8825 at 0°.

Propylidene dimethyl ether, obtained in a similar way, boils at 86—88°, and has a specific gravity of 0·8657 at 0°. G. T. M.

Action of Alcohol on Acraldehyde. By S. B. NEWBURY and E. M. CHAMOT (*Amer. Chem. J.*, **12**, 521—523).—The yield of isotriethylin, prepared according to the instructions given by Alsberg (*Jahrsber.*, 1864, 495), is very unsatisfactory and uncertain. The compound is best prepared by heating a mixture of acraldehyde (1 vol.) and absolute alcohol (3 vols.) at a temperature of 50° for five days. On shaking the product with a strong solution of calcium chloride, nearly the whole of it separates as an oily layer, which is dried and distilled in a vacuum. The purified product is a colourless liquid having a fruity odour, boiling at 85° under a pressure of 11 mm., and with decomposition at 180—185° under ordinary pressure, and having a specific gravity of 0·8959 at 0°. That it is isotriethylin or triethoxypropane is shown by its behaviour towards bromine and by analysis, but its properties are different from those ascribed to that compound by Alsberg. The position of the third ethoxy-group is not established, although the facts, that it readily decomposes on boiling, and that the difference between the boiling point of this substance and that of propylidene diethyl ether (compare preceding abstract) is nearly the same as that between the boiling points of acetal and ethoxyacetal, point to the third group as occupying the α-position, and to the constitution of the compound being $OEt{\cdot}CHMe{\cdot}CH(OEt)_2$. G. T. M.

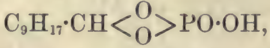
Action of Crotonaldehyde on Alcohol. By S. B. NEWBURY and W. S. CALKIN (*Amer. Chem. J.*, **12**, 523—525).—When mixtures of crotonaldehyde and alcohol are heated for a considerable time at temperatures up to 100°, the substances remain unchanged; combination, however, readily takes place when 60 grams of the former and 120 grams of the latter are heated, in a closed bottle for six days at 50°, with 30 grams of dry zinc chloride. The product, *triethoxybutane*, probably having the constitution

$$CH_2Me{\cdot}CH(OEt){\cdot}CH(OEt)_2,$$

is a colourless liquid of pleasant, fruity odour, boiling at 88—90°, under a reduced pressure of 150 mm., and with slight decomposition at 190° under ordinary pressures. The specific gravity of the liquid at 0° is 0·8825. G. T. M.

The Indian Grass Oils. By F. D. DODGE (*Amer. Chem. J.*, **12**, 553—564; compare Abstr., 1890, 231).—*Citronellic aldehyde* has a density of 0·8560 at 20°, and a rotatory power expressed by $[\alpha]_D = +4° 50'$. Its molecular refraction, $R\alpha = 47·60$, does not correspond with that calculated for an aldehyde having a hexatomic nucleus like the menthol series, but agrees with that calculated for the open chain formula $C_4H_9{\cdot}CH{:}CH{\cdot}C_3H_6{\cdot}COH$, or a similar one; hence, citronellic aldehyde must be regarded as a homologue of acraldehyde. On distilling the bromine additive product obtained from 100 grams of the aldehyde, 13 grams of cymene were obtained. This compound, however, was not formed when the aldehyde was treated with iodine and the product distilled, but a hydrocarbon boiling near 160° was obtained.

Citronellal-phosphoric acid is prepared as follows:—Phosphoric anhydride (5 grams) is covered with dry benzene (20 c.c.) and treated with water (0·55 gram) dissolved in ether (30 c.c.). A cake of metaphosphoric acid forms, and the greater part of the liquid is then poured off. To the residue, citronellic anhydride (10 grams) or citronella oil (20 grams) is added, and the containing vessel kept at a temperature of 70° for several hours. A concentrated solution of sodium carbonate is added until the solution becomes alkaline, the excess of oil separated, and the aqueous solution extracted with ether. Should the aqueous liquid remain coloured, a few drops of hydrochloric acid are added and the treatment with ether continued; this part of the process is repeated until the solution becomes colourless. Excess of concentrated hydrochloric acid is now added, the solution cooled and filtered, and the precipitated acid crystallised from warm dilute alcohol. It is sparingly soluble in water, from which it crystallises in prisms or long, flat needles, but dissolves readily in alcohol, from which, on slow evaporation of the solvent, it crystallises in square plates melting at 203°. It is a monobasic acid; the potassium salt crystallises in long needles and is very soluble in water; the sodium salt crystallises in forms resembling those of the free acid; the aniline salt and the quinoline salt both crystallise in white needles, the former melting at 165°. The acid is dextrorotatory, and most probably has the constitution



$$C_9H_{17}\cdot CH{<}{}^{O}_{O}{>}PO\cdot OH,$$

although the author has not succeeded in forming similarly constituted compounds from other aldehydes.

Lemon Grass Oil.—This substance is of uncertain botanical origin. It resembles citronella oil, insomuch as its chief constituent is an aldehyde, which may be isolated by treating the oil with sodium hydrogen sulphite. When 1000 grams of the dry sulphite are dissolved in 5 litres of hot water, 1 litre of the oil added whilst the solution is still warm, and the mixture vigorously stirred, a pasty mass of the hydrogen sulphite compound separates. On remaining for two or three hours, this precipitate dissolves, leaving a heavy, aqueous solution, containing the aldehyde, and a layer of residual oil (300 c.c.) above. In 24 hours, the solution is perfectly clear and may be siphoned off, filtered, and made strongly alkaline with sodium hydroxide. The supernatant layer of aldehyde is separated, filtered, and dried, when it forms a yellow oil (yield 65—68 per cent. of the grass oil taken) of pleasant, citrene odour, and is slightly volatile in a current of steam. It boils with gradual decomposition at 225°, has sp gr. = 0·8968 at 15·5°, is probably inactive, behaves with silver nitrate, phenylhydrazine, aniline, and paratoluidine like citronellic aldehyde; gives paramethylpropylbenzene on distillation with phosphoric anhydride, and cymene on distilling with steam the red oil obtained by the action of concentrated hydrochloric acid; on treatment with zinc-dust and acetic acid, it gives a product, which is probably the corresponding alcohol. Analysis of the aldehyde shows that it is isomeric with camphor, $C_{10}H_{16}O$. The above-mentioned aqueous liquid, containing the aldehyde, appears to be not merely a solution of the hydrogen sulphite compound in excess of sulphite, for a crystalline substance, having approximately the formula

$$C_{10}H_{16}O,2NaHSO_3,4Na_2SO_3,50H_2O,$$

can be separated from it, and further additions of the aldehyde to the solution do not cause the whole to precipitate as the sodium hydrogen sulphite compound. That portion of the lemon grass oil which does not combine with sodium hydrogen sulphite appears to contain a terpene as well as cymene.

Indian Geranium Oil.—Samples of this oil differed greatly in behaviour when distilled (compare Semmler, Abstr., 1890, 951).

G. T. M.

Action of Dilute Nitric Acid on Acetone. By S. B. Newbury and W. R. Orndorff (*Amer. Chem. J.*, **12**, 517—519; compare Debus, *Annalen*, **100**, 1, and Lubavin, *J. Russ. Chem. Soc.*, 1881, 329 and 495).—Acetone (1 kilo.) was added to nitric acid of sp. gr. 1·42 (1 kilo.), the mixture placed in tall glass cylinders, and a few drops of fuming nitric acid introduced at the bottom of each by means of a long pipette. In a few hours, bubbles of carbonic anhydride commenced to form, and the evolution of gas continued steadily for several weeks. At the end of two months, the liquid, which had a marked odour of hydrocyanic and acetic acids, was poured into a large dish and allowed to evaporate spontaneously. After several months, crystals of ammonium tetroxalate and free oxalic acid were found in the syrupy residue, which, on further concentration and cooling with ice, yielded a large quantity of crystals, the chief product of the reaction. These crystals agreed in every respect with hydroxyisobutyric acid, $OH·CMe_2·COOH$, and the original syrup furnished zinc hydroxyisobutyrate when boiled with zinc oxide. The mother liquor contained the zinc salt of another acid, but in quantity too small to admit of its identification. Neither pyruvic acid nor any other products of simple oxidation, without a breaking up of the acetone molecule, were formed in perceptible amounts. The production of hydrocyanic acid by the oxidation of organic substances has been explained by Hantzsch (*Annalen*, **222**, 65), and the formation of hydroxyisobutyric acid from acetone, hydrocyanic and hydrochloric acids, by Staedeler (*ibid.*, **111**, 320). G. T. M.

Action of Hydroxylamine on Isonitrosoketones. By R. Scholl (*Ber.*, **23**, 3578—3581).—When concentrated boiling aqueous solutions of hydroxylamine hydrochloride and isonitrosoacetone are mixed, the heat developed in the reaction causes the boiling to continue for some time. On neutralising with aqueous soda, a yellowish powder crystallises out, from which ether extracts methylglyoxime. The residue is practically insoluble in the common solvents, but dissolves in small quantity in boiling alcohol or water, separating from the latter in white, matted needles. It becomes brown at 180—200°, and explodes at 238—247°; it dissolves readily in mineral acids and solutions of sodium hydroxide and carbonate, and is reprecipitated on neutralisation. Its composition, as found from analysis and the determination of the molecular weight by Raoult's method, is $C_6H_9N_3O_3$. Its *hydrochloride*, $C_6H_9N_3O_3,HCl$, is formed by passing hydrogen chloride into the dry substance suspended in ether, and forms a hard, crystalline cake, which dissolves fairly readily in absolute alcohol, melts at 112—113°, and explodes at a higher temperature.

Isonitrosoacetophenone reacts with hydroxylamine in a similar manner, forming phenylglyoxime and a substance insoluble in ether and in all common organic solvents. It dissolves in soda with a yellow colour, and is reprecipitated by acids in white flakes having the composition $C_{16}H_{13}N_3O_3$. It also dissolves in hot hydrochloric acid, but separates out unaltered on cooling, and is probably identical with the compound obtained by Müller and Pechmann by the action of hydroxylamine on phenylglyoxal (Abstr., 1890, 51).

H. G. C.

Formation of Zinc Propionate by the Action of Carbonic Anhydride on Zinc Ethide. By R. Schmitt (*J. pr. Chem.* [2], **42**, 568—569).—Wanklyn (*Annalen*, **107**, 125) obtained sodium propionate by acting on zinc sodium ethide with carbonic anhydride. The author has succeeded in synthesising zinc propionate by acting on zinc ethide with liquid carbonic anhydride in an autoclave at 150—160°. At the same time there is a secondary reaction, by which some of the zinc propionate is decomposed into diethyl ketone and zinc carbonate.

A. G. B.

Preparation of Cerotic Acid. By T. Marie (*J. Pharm.* [5], **22**, 343—344).—125 grams of bees'-wax is heated with 3 litres of 93° alcohol for two hours. After cooling, the alcoholic jelly is poured off and the treatment with alcohol is repeated two or three times, and each time for a longer period, until the whole of the cerotic acid is removed. The alcoholic portions are united, filtered, and distilled with a little potash, to retain the volatile acids which have been removed from the wax, and the distillate serves to dissolve the impure acid upon the filter. This solution being heated to boiling, the myricin contained forms minute droplets, which are deposited on cooling quietly, and adhere closely to the flask. The supernatant jelly is poured on to a filter and washed with a small quantity of alcohol. After three such treatments and two crystallisations from alcohol, the acid is colourless, and melts at 76—77°; it is then almost pure. If converted into the lead salt, according to Brodie's method, ether extracts but an insignificant amount of matter, and the regenerated acid melts at 78°.

J. T.

Formation of Ethereal Salts by Means of Ethyl Chlorocarbonate. By R. Otto and W. Otto (*Arch. Pharm.*, **228**, 500—516).—When ethyl chlorocarbonate is gradually added to sodium formate covered with about twice its volume of alcohol, carbonic anhydride is at once evolved; after remaining some time at the ordinary temperature, the liquid contains, besides sodium chloride and ethyl carbonate, ethyl formate and free formic acid, with perhaps some free hydrochloric acid. To separate the ethyl formate, the solution is supersaturated with sodium carbonate, water added, if necessary, and sodium chloride to reduce the solubility of the formate, which is then siphoned off, placed over ignited potash, and purified by fractional distillation. An intermediate carboxy-compound is supposed to be formed during the reaction, thus:—$H{\cdot}COONa + ClCOOEt = NaCl + HCO{\cdot}O{\cdot}COOEt$; this ethylic carboformate is partly decomposed directly, thus:—$HCO{\cdot}O{\cdot}COOEt = CO_2 + HCOOEt$ (I), and the remaining part under the action of water from the alcohol gives $HCO{\cdot}O{\cdot}COOEt + H_2O = CO_2 + EtHO + HCOOH$ (II). If alcohol and water be excluded, equation (I) still holds good, but the remaining part of the carboformate is decomposed as follows:—$2HCO{\cdot}O{\cdot}COOEt = Et_2CO_3 + CO_2 + (HCO)_2O$ (III), the latter immediately decomposing into formic acid and carbon monoxide. Sodium acetate treated with alcohol and ethyl chlorocarbonate similarly yields acetic anhydride and also ethyl carbonate, showing that a reaction analogous to (III) holds good here, thus:—$2MeCO{\cdot}O{\cdot}COOEt = (MeCO)_2O + Et_2CO_3 + CO_2$. Calcium propionate, sodium isovalerate, and sodium stearate yielded analogous ethyl compounds. Three monobasic acids of the aromatic series were next examined. Sodium benzoate when acted on by ethyl chlorocarbonate in presence of alcohol formed essentially ethyl benzoate and benzoic anhydride, whilst when water is excluded ethyl carbonate is also formed. Here also an intermediate carboxy-compound, $C_6H_5CO{\cdot}O{\cdot}COOEt$, is supposed to enter into the reaction, analogous to the compound formed with formates. Potassium metatoluate yielded ethyl metatoluate and a larger amount of metatoluic anhydride. Next, the sodium salt of an isomeride of the last acid, phenylacetic acid, was treated. This yielded ethyl phenylacetate, but no anhydride, and in this respect resembles the fatty series. Of bibasic acids, the potassium salt of oxalic acid yielded scarcely any ethyl oxalate in presence of alcohol, owing to the precipitation of the salt from its aqueous solution by this alcohol. In the absence of alcohol, a small quantity of ethyl oxalate was formed after some days. With potassium succinate, the reaction was very energetic. Ethyl potassium succinate was produced, and a little ethyl carbonate. In the bibasic aromatic series, potassium phthalate was employed. Ethyl phthalate was formed, but much phthalic acid was re-formed. Finally, sodium salicylate yielded a little ethyl salicylate and carbonate, and again much of the salicylic acid was regenerated.

J. T.

Pimelic Acids. By C. A. Bischoff and K. Jaunsnicker (*Ber.*, **23**, 3399—3409).—Symmetrical dimethylglutaric acid (m. p. 105°), from methyl iodide and ethyl isobutenyltricarboxylate, is identical with the "trimethylsuccinic acid" from ethyl methylmalonate and ethyl bromisobutyrate, and also with the acid from ethyl methylmalonate and methyl iodide, as well as with Zelinsky's acid (compare Abstr., 1890, 132). On heating with hydrochloric acid in a sealed tube for 24 hours at 230—250°, the para-acid is formed (*loc. cit.*).

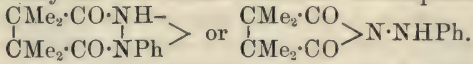
After the separation of dimethylglutaric acid from the product of the action of methyl iodide on ethyl isobutenyltricarboxylate, the lower fraction, boiling at 200—245°, yields a compound which has the formula $C_6H_{10}O_4$; two preparations showed the melting points 88—92° and 103—113°, whilst the electrolytic conductivities, $[\mu]\infty = 353$, are $\kappa = 0{\cdot}0114$ and $0{\cdot}0112$ respectively. This acid appears to occupy a position in the series intermediate between methylsuccinic acid and antidimethylsuccinic acid; the formula points to its being an isomeric dimethylsuccinic or ethylsuccinic acid. The paper concludes with a systematic comparison of the acids obtained: (I) by the oxidation of castor oil; (II) from amylene bromide (trimethylsuccinic acid); (III) from methylene iodide and ethyl methylmalonate (dimethylglutaric acid); (IV) from methyl iodide and ethyl isobutenyltricarboxylate. J. B. T.

Ethyldimethylsuccinic Acid. By C. A. BISCHOFF and N. MINTZ (*Ber.*, **23**, 3410—3413).—*Ethyldimethylsuccinic acid*,

$$COOH{\cdot}CHEt{\cdot}CMe_2{\cdot}COOH,$$

is prepared by heating ethyl orthobromisobutyrate with ethyl sodium ethylmalonate in xylene solution at 180—190° for 21 hours, under a pressure of 3 atmospheres the product appears to consist of a mixture of two ethereal salts; it is hydrolysed with potash, and, after purification, the pure acid crystallises from benzene or water in long, concentric prisms, melts at 139° (uncorr.), and is insoluble in light petroleum, carbon bisulphide, and xylene, but readily dissolves in ether, acetone, chloroform, or glacial acetic acid. The electrolytic conductivity is $\kappa = 0{\cdot}0582$ $[\mu\infty = 351]$. The *barium* and *silver* salts have been prepared; the latter is crystalline, and insoluble in water. J. B. T.

Tetramethylsuccinic Acid. By K. AUWERS and J. A. GARDNER (*Ber.*, **23**, 3622—3625).—*Tetramethylsuccinimide*, $C_6H_{12}{<}^{CO}_{CO}{>}NH$, is prepared by dissolving tetramethylsuccinic acid in aqueous ammonia; the solution is evaporated, and the residue heated at 230° for several hours in a sealed tube; the compound crystallises from a mixture of benzene and light petroleum in flat needles, melts at 187°, and may be distilled without decomposition; it may also be prepared by heating the anhydride with aqueous ammonia at 100°. The *phenylimide*, $C_6H_{12}{<}^{CO}_{CO}{>}NPh$, is obtained by the action of aniline on the acid or anhydride, and crystallises from dilute alcohol, or a mixture of benzene and light petroleum, in needles, melts at 88°, and is insoluble in cold water.

By treating the acid with phenylhydrazine, only one compound is obtained, which crystallises in flat, lustrous needles melting at 124°; it may be volatilised without decomposition, and has the formula  $\begin{array}{l}CMe_2{\cdot}CO{\cdot}NH-\\ CMe_2{\cdot}CO{\cdot}NPh\end{array}{>}$ or $\begin{array}{l}CMe_2{\cdot}CO\\ CMe_2{\cdot}CO\end{array}{>}N{\cdot}NHPh$. The anhydride is the sole product formed by the action of phosphorus pentachloride on tetramethylsuccinic acid or its salts. With resorcinol, the acid yields a fluoresceïn derivative, which dissolves in acids with a red coloration, and a green fluorescence. J. B. T.

Homologues of Maleïc Acid. By C. A. Bischoff (*Ber.*, **23**, 3414—3423).—A reply to Anschütz's paper (this vol., p. 176). The affinity of sodium for oxygen is greater than that of hydrogen, consequently, in hydrogen sodium carbonate the oxygen of the group ONa is at a greater distance from the carbon atom than that of the group OH; in carbonic acid, however, the oxygen atoms of both hydroxyl groups are equally distant from the carbon atom; hence collisions readily occur, and the compound decomposes into water and carbonic anhydride. The same principle is illustrated by reference to acetaldehyde and chloral hydrate. A comparison is then instituted, by means of models, between succinic and maleïc acids, on the one hand, and symmetrical dimethylsuccinic and pyrocinchonic acids on the other; it is shown that the hydroxyl groups approach as closely as in the case of carbonic acid. As regards the influence of the other atoms or groups in the molecule, the elimination of two hydrogen atoms from succinic acid, or their displacement by two methyl groups, facilitates the formation of anhydrides. It is proposed to determine what influence the ethyl and methyl groups have on the elimination of water from maleïc acid.

By the action of bromine on propenyltricarboxylic acid, carbonic anhydride and hydrogen bromide are evolved, and the resulting succinic acid derivative, $COOH\cdot CHMe\cdot CHBr\cdot COOH$, yields citraconic acid on distillation, whilst by the action of hydrochloric acid at 160°, mesaconic acid is formed. Ethylmaleïc and ethylfumaric acids are prepared in a similar manner from butenyltricarboxylic acid. Disubstituted maleïc acids may be obtained from the corresponding succinic anhydrides (compare Bischoff and Voit, Abstr., 1890, 743).

Ethylmethylmaleïc anhydride is a colourless oil which boils at 237°, is soluble in potash, and is reprecipitated unchanged by hydrochloric acid. Xeronic anhydride is formed in the same way from diethylsuccinic anhydride. J. B. T.

Combination of Malic Acid with Potassium Sodium Molybdate and with Acid Sodium Molybdate. By D. Gernez (*Compt. rend.*, **111**, 792—794).—The salts were added gradually to a solution of a definite quantity of malic acid, the total volume of liquid being kept constant, and the rotatory power was determined in the manner previously described. With potassium sodium molybdate,

$$K_2O,2Na_2O,3MoO_3,14H_2O,$$

the lævorotatory power at first increases in proportion to the quantity of salt added, and attains a maximum when three equivalents of acid are present for each equivalent of salt. Subsequent variations in rotatory power indicate the formation of compounds containing respectively 3 equivalents of acid and 2 of the salt, 3 equivalents of the acid and 3·5 of the salt, and 3 of the acid and 6·5 of the salt.

With malic acid and the acid sodium molybdate, $3Na_2O,7MoO_3$, the variations in rotation indicate the formation of a compound of 3 equivalents of acid and 1 of the salt, and a compound of equal equivalents of the acid and the salt, the phenomena being analogous to those observed with ammonium molybdate, although the rotatory powers are somewhat larger. C. H. B.

Ethyl Isobutenyltricarboxylate. By C. A. Bischoff (*Ber.*, **23**, 3395—3399).—Auwers and Jackson have shown (Abstr., 1890, 1098) that the compound obtained by the action of ethyl methylmalonate on ethyl bromisobutyrate has the formula

$$CMe(COOEt)_2{\cdot}CH_2{\cdot}CHMe{\cdot}COOEt,$$

and, when hydrolysed, yields dimethylglutaric acid with elimination of carbonic anhydride. The author had, however, previously prepared, in a similar manner, an identical compound from ethyl isobutenyltricarboxylate and methyl iodide, which he considered to be trimethylsuccinic acid. Further investigation has shown that "ethyl isobutenyltricarboxylate" consists of two compounds of the formulæ $COOEt{\cdot}CMe_2{\cdot}CH(COOEt)_2$ and $COOEt{\cdot}CHMe{\cdot}CH_2{\cdot}CH(COOEt)_2$ respectively, and that, on hydrolysis and elimination of carbonic anhydride, it yields a mixture of α-methylglutaric acid and dimethylsuccinic acid, which may be separated by fractional distillation. No trimethylsuccinic acid could be isolated from the methyl iodide and ethyl isobutenyltricarboxylate product, which, therefore, consists only of dimethylglutaric acid. Trimethylsuccinic acid has, however, previously been prepared, and is known by the name isopimelic acid (compare this vol. p. 289). J. B. T.

Action of Nitrous Acid on Amido-derivatives. By E. A. Klobbie (*Rec. Trav. Chim.*, **9**, 134—154).—The action of nitrous acid on the following compounds has been investigated by the author in order to determine the influence on the action of the accumulation of negative groups in the amido-derivative.

Nitrous acid acts on methyl amidoformate to form methyl alcohol, with evolution of nitrogen and carbonic anhydride. With the same reagent, ethyl methylamidoformate yields a nitroso-derivative, $NO{\cdot}NMe{\cdot}COOEt$, which is a red liquid of sp. gr. 1·133 at 15°, boiling at 70° under a pressure of 27 mm. Methyl methylamidoformate also forms a nitroso-compound, $NO{\cdot}NMe{\cdot}COOMe$, having similar properties to the last-named compound. Methyl ethylamidoformate, in aqueous solution, is acted on by a current of nitrogen trioxide, and forms a nitroso-derivative, $NO{\cdot}NEt{\cdot}COOMe$, which is a dark-orange liquid of sp. gr. 1·143 at 15°.

Methyl acetylamidoformate, which is obtained by the action of ethyl methylcarbamate on acetic chloride at a moderate heat, is a crystalline substance which melts at 93°, and is very soluble in water, alcohol, ether, chloroform, and crystallises easily from benzene. On treating an aqueous solution of this substance with nitrogen trioxide, decomposition occurs according to the equation $CH_3{\cdot}CO{\cdot}NH{\cdot}COOMe + HNO_2 = CH_3{\cdot}COOH + N_2 + CO_2 + MeOH$.

Methyl imidodiformate, $NH(COOMe)_2$, is prepared by mixing methyl chloroformate (1 mol.) and methyl amidoformate (1 mol.) with 4 parts of toluene, and acting on the mixture with sodium (1 mol.). After filtration of the product, the unattacked sodium is removed from the residue, and the mass is treated with dilute sulphuric acid, which yields up to toluene a crystalline substance melting at 134°; this is very soluble in water, alcohol, acetone, and chloroform, slightly soluble in ether, and almost insoluble in light petroleum. Nitrous acid has no action whatever on this substance, neither has it any action on ethyl dimethylamidoformate or on the corresponding methyl derivative.

Ethyl methylacetylamidoformate cannot be made by acting on ethyl nitrosomethylamidoformate with acetic anhydride or on ethyl methylcarbamate with the same reagent; but in presence of zinc chloride, the reaction occurs in the latter case. Ethyl methylcarbamate (60 grams), acetic anhydride (30 grams), and zinc chloride (4 grams) are heated for some minutes at the boiling point of the mixture until a yellow coloration is produced; the liquid is extracted with ether, and yields, on distillation, a liquid which boils at 189° (corr.) and has a sp. gr. 1·083 at 15°, its melting point being 8—9°. Nitrous acid does not act on this substance.

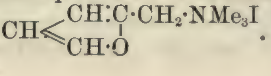
Ethyl nitrosomethylamidoformate, $NO{\cdot}NMe{\cdot}COOEt$. This red liquid is dissolved in all proportions by alcohol, ether, and benzene, and is but slightly soluble in water although distillable with steam. The analogy in the composition of this substance to that of ethyl nitromethylcarbamate led the author to treat it with ammonia, which does not react except in the presence of water, when it forms ethyl carbamate and methyl alcohol with evolution of nitrogen, pointing to the formation of a compound $NHMe{\cdot}NO$, which immediately decomposes. Aqueous solutions of mono- and of di-methylamine react similarly to form the compounds $NHMe{\cdot}COOEt$ and $NMe_2{\cdot}COOEt$, boiling at 165° and 147° (corr.) respectively. Ethyl ethylcarbamate reacts on the substance with formation of nitrogen, carbonic anhydride, and ethyl methylamidoformate. In contradistinction to the nitro-derivative, $NO_2{\cdot}NMe{\cdot}COOEt$, which yields with ammonia an acid nitramine, $NHMe{\cdot}NO_2$, the nitroso-derivative furnishes only decomposition products of a corresponding nitrosamine, $NHMe{\cdot}NO$; the author endeavoured to isolate its potassium and barium salts, but was unsuccessful. Mineral acids decompose ethyl nitrosomethylamidoformate with substitution of hydrogen for the group NO; oxidation is effected by an acid solution of potassium permanganate, but the nitroso-compound is not converted into the nitro-compound.

By reduction of ethyl nitrosomethylamidoformate with zinc-dust and acetic acid, a colourless solution is formed, having strong reducing properties, and probably containing the hydrazine, $NH_2{\cdot}NMe{\cdot}COOEt$; but this the author was unable to isolate, or to obtain a condensation product of, with aldehydes. At the same time, a small quantity of a white powder, which melts at 127—128° and sublimes at 180°, is obtained; this appears to be ethyl dimethyltetrazonedicarboxylate, $N_2(NMe{\cdot}COOEt)_2$. This substance is also formed when the liquid resulting from the reduction of a solution of the nitroso-compound is oxidised by potassium permanganate, ferric chloride, or bromine water, the last reagent affording the better yield. It is soluble in alcohol, benzene, acetone, or acetic acid, but is insoluble in water, ether, light petroleum, or solutions of the aqueous hydroxides or the mineral acids.

By similar reactions, methyl nitrosoamidoformate yields the tetrazone, $N_2(NMe{\cdot}COOMe)_2$, which melts at 184°; and methyl nitrosomethylamidoformate, the corresponding derivative, $N_2(NEt{\cdot}COOMe)_2$, melting at 88—89°. The author concludes with theoretical speculations as to the rationale of the reactions. T. G. N.

Reduction of Glycuronic Acid by Sodium Amalgam. By H. Thierfelder (*Zeit. physiol. Chem.*, **15**, 71—76; compare Abstr., 1887, 717; 1889, 337).—Pure sodium glycuronate was dissolved in five times its weight of water in a loosely-stoppered flask, and a little 2·5 per cent. sodium amalgam added, when hydrogen was evolved; the liquid was then neutralised by sulphuric acid, and more amalgam added; after some weeks, all the glycuronic acid had disappeared. The liquid was filtered, acidified with sulphuric acid, and excess of alcohol added; the sodium sulphate thus precipitated was filtered off, and the filtrate evaporated to dryness on the water-bath, with the addition of barium carbonate. The residue was taken up with water, filtered, concentrated, acidified with sulphuric acid, and extracted with a mixture of alcohol and ether. The extract was evaporated to a syrup, when, after a short time, small, colourless crystals were deposited; on recrystallisation from water, rhombic crystals, 1 cm. long, were obtained. Details are given relating to the measurement of the crystals. The substance has a slightly sweet taste, is readily soluble in water, but only sparingly in alcohol. It melts at 178—180°, and has the composition $C_6H_{12}O_7$. Its barium, calcium, and potassium salts were examined. Examination of the solubilities and circular polarisation (the free acid is optically inactive) excluded gluconic and galactonic acids. It does not reduce Fehling's solution, so it cannot be mannitic acid. Similar considerations lead to the conclusion that it is not either of the three mannonic acids: so it is not the same as any known acid with the formula $C_6H_{12}O_9$; the nature of the new acid must therefore be the subject of renewed investigation.

W. D. H.

Action of Methyl Iodide on Furfurylamine. By M. Zenoni (*Gazzetta*, **20**, 513—517).—Furfurylamine may be readily prepared in considerable quantities by reducing furfuraldoxime with alcohol and sodium. The yield is 20 per cent. When a solution of furfurylamine (1 part), in twice its volume of methyl alcohol, is heated with methyl iodide (5 parts), the product, after purification, is a white, crystalline powder which melts at 118—120°, and has the composition $C_8H_{14}ONI$. This substance has the general properties of the iodides of the organic bases. It is soluble in water and alcohol, and is reprecipitated from the aqueous solution on addition of potash. Its constitution is probably  $CH{<}\begin{matrix}CH{:}C{\cdot}CH_2{\cdot}NMe_3I\\ CH{\cdot}O\end{matrix}$. The corresponding *hydroxide* is formed by the action of moist silver oxide on the iodide, and may be obtained as a deliquescent, crystalline mass which absorbs carbonic anhydride from the air. The *chloride* is obtained by treating the iodide with fresh moist silver chloride. It is a deliquescent crystalline compound. The *aurochloride*, $C_8H_{14}ONCl,AuCl_3$, *platinochloride*, and *picrate* are yellow, crystalline compounds; the latter melts with decomposition at about 180°.

On distilling the hydroxide, an alkaline liquid having an odour resembling that of trimethylamine and an oily product, which is resinified by hydrochloric acid, pass over. S. B. A. A.

Action of Acid Chlorides on Bases in presence of Alkalis. By C. SCHOTTEN (*Ber.*, **23**, 3430—3431).—Polemical remarks on Marckwald's paper (this vol., p. 181).

Pyromucic and Dehydromucic Acids. By M. ZENONI (*Gazzetta*, **20**, 517—520).—The author further confirms the results obtained by Oliveri and Peratoner (Abstr., 1890, 1242); both the solid product of the distillation of mucic acid and the mother liquor, after sufficient purification, yielding ordinary pyromucic acid melting at 132—133°. In the course of the experiments, a considerable quantity of a reddish-yellow residue, consisting of dehydromucic acid, was obtained. This compound would appear to be more particularly formed when mucic acid is distilled at a low temperature. The *methyl* salt of this acid, $C_6H_2O_5Me_2$, crystallises from water in large, white needles, and melts at 112°. It is not affected by treatment with bromine or nitric acid.

The *hydrazone*, $C_4OH_3{\cdot}CO{\cdot}N_2H_2Ph$, obtained by heating the theoretical quantities of pyromucic acid and phenylhydrazine, crystallises in white needles, and melts at 142—143°; its solution in concentrated sulphuric acid is coloured deep violet on the addition of ferric chloride. S. B. A. A.

Bromobenzonitriles. By M. SCHÖPFF (*Ber.*, **23**, 3435—3440).—The best method of preparing these nitriles is to distil the corresponding bromobenzoic acids with lead thiocyanate. The yield of nitrile appears to be better the lower the melting point of the acid.

Orthobromobenzonitrile is formed by distilling orthobromobenzoic acid (20 grams) with lead thiocyanate (36 grams) and purifying the product by steam-distillation. It crystallises in white needles, melts at 51°, and boils at 251—253° (uncor.) under 754 mm. pressure. It is easily soluble in hot water and alcohol, and has a characteristic odour resembling that of benzaldehyde and benzonitrile. The yield amounts to 45 per cent. of the theoretical. Orthobromobenzonitrile can also be obtained by distilling orthobromobenzamide with phosphoric anhydride.

Orthobromobenzoic chloride, prepared by the action of equal weights of phosphorus pentachloride and orthobromobenzoic acid, is a colourless liquid which boils at 241—243° (uncorr.) under 757 mm. pressure, and gradually solidifies after a time. It has an odour resembling that of benzoic chloride, but less pungent. It is slowly decomposed by cold water, more quickly by hot water, and reacts very energetically with ammonia. *Orthobromobenzamide*, prepared by treating the chloride with finely powdered ammonium carbonate at the temperature of the water-bath, crystallises from hot water or alcohol in long, hard needles, melts at 156° when heated rapidly, and sublimes above 100°.

Metabromobenzonitrile is obtained by distilling metabromobenzoic acid with lead thiocyanate, and is extracted from the distillate with ether, after the unaltered acid has been neutralised with dilute ammonia. It crystallises in needles, melts at 38°, and boils at 225°.

Parabromobenzonitrile is best prepared from parabromobenzamide by distillation with phosphoric anhydride and purification of the product by steam-distillation. Owing to the high melting point of parabromobenzoic acid, only 33 per cent. of the theoretical yield is obtained on distilling it with lead thiocyanate. It crystallises from hot water or alcohol in slender, white needles, melts at 113°, is somewhat less volatile with steam than the ortho-compound, sublimes in white needles, and boils at 235—237° (uncorr.).

When orthobromobenzonitrile is nitrated and the product hydrolysed, it is converted into orthobromometanitrobenzoic acid melting at 179—180°. Parabromobenzonitrile, when treated in the same way, yields parabromometanitrobenzoic acid melting at 199°. The nitration is best effected by means of a mixture of potassium nitrate and sulphuric acid. By employing fuming nitric acid, the nitrile remains unaltered.

Orthobromometanitrobenzonitrile crystallises from water in needles, melts at 117°, and is volatile with steam.

Parabromometanitrobenzonitrile crystallises in white needles, melts at 120°, is not so volatile with steam as the ortho-compound, dissolves easily in hot water, alcohol, and acetone, less easily in chloroform and benzene, and is insoluble in light petroleum. The amide is alone formed if the parabromometanitrobenzonitrile is allowed to remain in the nitric acid mixture for a short time. The amide forms colourless needles, melts at 156°, and is not volatile with steam.

E. C. R.

Action of Methylchloroform on Phenol in presence of Potassium and Sodium Hydroxides. By P. BIGINELLI (*Chem. Centr.*, 1890, ii, 620; from *Ann. Chim. Farm.*, **12**, 65—68).—With the object of generalising the reaction between chloroform and phenol in presence of potash, by which hydroxyaldehydes are produced, the author substituted methylchloroform for chloroform, when, if the reaction were similar, hydroxybenzyl methyl ketone, should be produced. Instead of this, a substance of the formula $C_{14}H_{12}O_2$ is formed, which the author regards as diphenylethylidene ether, $CH_2{:}C(OPh)_2$. It is very soluble in ether, and melts at 95—96°. It does not dissolve in potash, neither does it react with phenylhydrazine. With bromine water, a compound of the formula $C_{14}H_{12}Br_2O_2$ is formed without any hydrogen bromide being produced. It crystallises in plates which melt at 125°.

A second substance is formed in the above reaction, a liquid, which distils with steam; after drying over sulphuric acid, the analysis gave the formula $C_8H_8O_2$, which agrees with that of orthohydroxy-acetophenone. It does not, however, appear to combine with phenylhydrazine, or with hydroxylamine. By treating it in methyl alcohol solution with sodium amalgam, a crystalline substance smelling strongly of oil of roses was obtained. J. W. L.

Tetrachlorophenol. By L. Hugouneng (*Bull. Soc. Chim.* [3], **4**, 8—9; compare Abstr., 1890, 241).—Tetrachloranisoïl is heated with hydriodic acid of sp. gr. 1·5 (4 parts) in sealed tubes at 145—148° for 20 hours, and from the solution of the product in aqueous soda tetrachlorophenol is precipitated on the addition of hydrochloric acid, and after washing and drying, is crystallised from light petroleum. Thus prepared, it forms white needles, melts at 152°, is sublimable, and boils at 278° with decomposition. Tetrachlorophenol is insoluble in water, but dissolves in organic solvents; the alcoholic solution decomposes carbonates and seems not to be poisonous. A mixture of nitric and sulphuric acids decomposes the substance with formation of chloronitroquinones. The author has prepared the acetyl derivative, C_6HCl_4Ac, and the ammonium, silver, lead, and copper salts.

T. G. N.

Constitution of Thymoquinone and β-Hydroxythymoquinone Derivatives. (By G. Mazzara, *Gazzetta*, **20**, 481—485).—In a previous paper (see Abstr., 1890, 965), the preparation of β-hydroxythymoquinone from carvacrol [$Me : O_2 : Pr : OH = 1 : 3 : 6 : 4 : 5$] was described. To characterise this compound more fully, the anilide and toluidide [$NHPh$ or $NH{\cdot}C_6H_4Me = 2$] were prepared by boiling the alcoholic solution of the quinone with aniline, or toluidine, respectively. The *anilide* crystallises from alcohol in minute, deep-blue scales, dissolves in alkaline hydroxides forming a violet solution, and melts at 185—187°, whilst the isomeride derived from α-hydroxythymoquinone melts at 135°. The *toluidide* also crystallises in blue scales which melt, however, at 196—197°; whereas the corresponding isomeride melts at 165°.

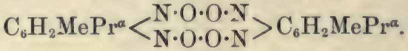
It is noticeable that in compounds derived from thymol, the melting point is lowered in passing from the nitro- to the dinitro-derivatives, and from the hydroxythymoquinone to either the anilide or toluidide, whilst the reverse occurs in the corresponding compounds from carvacrol.

The author regards it as finally established that the β-bromo- and β-bromohydro-thymoquinone are really α-derivatives [$Br = 2$].

S. B. A. A.

Thymoquinone Dioxime. By F. Kehrmann and J. Messinger (*Ber.*, **23**, 3557—3564).—As already shortly mentioned (Abstr., 1890, 1403), thymoquinone dioxime, $C_6H_2Pr^aMe(NOH)_2$, may be obtained by the action of hydroxylamine on thymoquinone monoxime (nitrosothymol). In order to prepare it, a hot saturated alcoholic solution of the latter is boiled with double the theoretical quantity of hydroxylamine hydrochloride, the acid set free being nearly neutralised from time to time. The resulting crystalline powder is dissolved in warm soda, precipitated by acetic acid, and recrystallised from boiling alcohol. It forms yellowish-white granules, which are insoluble in water and ammonia, sparingly soluble in cold alcohol and acetic acid, and readily in solutions of the caustic alkalis, forming salts which are decomposed by carbonic anhydride. It becomes brown at 200° and decomposes with evolution of gas at 235°. Its solution in soda has the colour of an alkaline solution of potassium ferricyanide, and on the addition of very concentrated alkali, the *sodium* salt separates out in golden-yellow, prismatic crystals which are very soluble in water. The dioxime is not identical with the polythymoquinone dioxime described by Liebermann and Ilinski (Abstr., 1886, 239).

When an alkaline solution of potassium ferricyanide is added to a similar solution of thymoquinone dioxime, a green, flocculent precipitate of *dinitrosocumene* separates. It has an odour resembling that of iodine and of thymoquinone, and is volatile with steam, undergoing considerable decomposition at the same time. It is soluble in alcohol, ether, and acetic acid with an intense green colour, the solutions also rapidly undergoing decomposition. In the dry state, it is fairly stable, and melts at 72° to a greenish-yellow liquid which then solidifies and again melts at 130° with decomposition. The authors regard it as most probable that the compound has the formula



$$C_6H_2MePr^{\alpha}<\begin{matrix}N\cdot O\cdot O\cdot N\\N\cdot O\cdot O\cdot N\end{matrix}>C_6H_2MePr^{\alpha}.$$

When boiled with nitric acid of sp. gr. 1·35, it is converted into *paradinitrocumene*, $C_6H_2MePr^{\alpha}(NO_2)_2$, which crystallises from hot dilute alcohol in large, colourless, thick prisms, melts at 77—78°, and is readily soluble in alcohol, ether, acetic acid, and benzene. When reduced with tin and hydrochloric acid, it yields *paradiamidocumene*, which may be more readily obtained from thymoquinone dioxime by suspending it in alcohol, warming with an excess of stannous chloride and hydrochloric acid, evaporating the alcohol, diluting with water, and adding aqueous soda. The base is extracted with ether, and the solution agitated with concentrated hydrochloric acid as long as separation of the hydrochloride takes place. The latter is dissolved in the least possible quantity of hot water, and concentrated hydrochloric acid added; it then separates in well-developed, colourless, four-sided plates, which are quite stable in the air, whereas the free base readily undergoes oxidation. The diamidocumene hydrochloride obtained by Liebermann and Ilinski (*loc. cit.*) is identical with the foregoing, but the latter investigators do not appear to have obtained it quite pure.

On boiling paradiamidocumene hydrochloride with acetic anhydride and anhydrous sodium acetate, it yields the *diacetyl* compound, $C_{14}H_{20}N_2O_2$, crystallising in slender, white, silky needles and melting at 260°.
H. G. C.

Cholesterol. By K. OBERMÜLLER (*Zeit. physiol. Chem.*, **15**, 37—48).—Two formulæ, $C_{26}H_{44}O$ and $C_{27}H_{46}O$ (Reinitzer, Abstr., 1888, 1076), have been ascribed to cholesterol (cholesterin). The chief object of the present research was, by the analysis of certain cholesterol compounds, to determine which is the correct one. The general result of the analyses is that Reinitzer's formula is correct. The following compounds were prepared:—

Potassium cholesteroxide, $C_{27}H_{45}OK$, was prepared by placing potassium in an ethereal solution of cholesterol. It agrees in all its properties with Reinitzer's sodium cholesteroxide.

Cholesteryl propionate, $C_{27}H_{45}\cdot C_3H_5O_2$, was prepared by heating a mixture of cholesterol with propionic anhydride on the water-bath for half-an-hour; on cooling, it sets to a fatty mass; this is extracted with ether, and the propionate precipitated from the extract by alcohol in the form of rhombic plates; melting point 98°. It is easily soluble in ether, benzene, and carbon bisulphide, sparingly soluble in alcohol. After fusion, there is, on cooling, a play of colours observed, blue, green, orange, and red, in the order named, by reflected light; the complementary colours are seen by transmitted light. In order to use this reaction as a test for cholesterol, the latter must first be obtained in a pure condition; it may be most readily freed from the fats with which it is usually mixed by the method of saponification before described (Abstr., 1890, 1474).

Cholesteryl benzoate, $C_{27}H_{45}\cdot C_7H_5O_2$.—This is best prepared by the action of benzoic chloride on cholesterol; and this preparation may be used for the quantitative estimation of cholesterol. The crystals are plates which show two melting points, namely, 145° and 178°. A compound with similar properties was prepared from isocholesterol.

Cholesteryl phthalate, $C_6H_4(COO\cdot C_{27}H_{45})_2$, was prepared by heating phthalic anhydride and cholesterol at 180°, and crystals obtained by the addition of alcohol to a hot ethereal solution. It is sparingly soluble in cold ether; melting point 182·5°.

Cholesteryl benzyl ether, $C_{27}H_{45}\cdot O\cdot C_7H_7$, prepared by heating sodium cholesteroxide and benzyl chloride at 100°, was crystallised from an alcoholic-ethereal solution in thin plates melting at 78°.

Cholesteryl propionate dibromide, $C_{27}H_{45}Br_2\cdot C_3H_5O_2$.—This additive product is similar to that prepared previously by Wislicenus and Moldenbauer, $C_{27}H_{46}Br_2O$ (*Annalen*, **146**, 178), by the action of bromine dissolved in carbon bisulphide on pure cholesterol, and to that prepared by Reinitzer (*Wiener Monatsh.*, 1888, Heft 5), by the action of bromine on cholesteryl acetate. This substance is important, as the relation between carbon and bromine gives a key to the formula of cholesterol. *Cholesteryl bromobenzoate*, $C_7H_4BrO_2\cdot C_{27}H_{45}$, was also prepared and analysed. W. D. H.

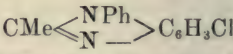
Derivatives of Diphenylamine. By O. ERNST (*Ber.*, **23**, 3423—3430).—*Amidochlorodiphenylamine*,

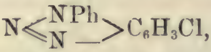
$$NHPh\cdot C_6H_3Cl\cdot NH_2\ [NHPh : NH_2 : Cl = 1 : 2 : 5],$$

is prepared by the reduction of the nitro-compound with stannous chloride, tin, and hydrochloric acid in alcoholic solution; it crystallises from alcohol in long, colourless needles, melts at 99°, and is readily soluble in ether, benzene, and chloroform. The *picrate* crystallises in yellowish-brown plates. The *acetyl derivative*,

$$NHPh\cdot C_6H_3Cl\cdot NHAc,$$

is formed by the action of the calculated quantity of acetic anhydride at 100°, and crystallises from alcohol in silky, lustrous needles which melt at 150°.

Ethenylorthamidochlorodiphenylamine,  $\mathrm{CMe}<\begin{smallmatrix}\mathrm{NPh}\\ \mathrm{N}\text{—}\end{smallmatrix}>\mathrm{C_6H_3Cl}$, is obtained on boiling the amido-compound with excess of acetic anhydride; it crystallises with difficulty in small, colourless needles. The *platinochloride* crystallises from alcohol in long, brown needles.

Phenylazimidochlorobenzene,  $\mathrm{N}<\begin{smallmatrix}\mathrm{NPh}\\ \mathrm{N}\text{—}\end{smallmatrix}>\mathrm{C_6H_3Cl}$, is prepared by the action of nitrous acid on orthamidochlorodiphenylamine; it crystallises from alcohol in colourless, lustrous needles, and melts at 128°.

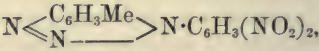
By the oxidation of an acid solution of amidochlorodiphenylamine with ferric chloride, a violet-red dye is produced, the *hydrochloride* of which crystallises in yellowish-green, metallic, lustrous needles; the *picrate* is deposited in dark-green needles; the *sulphate* resembles the hydrochloride. The free *base* is obtained by the action of ammonia on the salts, as a brownish-red, crystalline precipitate.

On heating orthamidochlorodiphenylamine with an equal molecular proportion of aniline hydrochloride at 200°, a deep-blue colouring matter is formed; dilute solutions exhibit a copper-red fluorescence. The addition of ammonia changes the colour to reddish-violet with yellow-red fluorescence. A similar substance is formed by heating orthamidochlorodiphenylamine hydrochloride alone. This compound probably belongs to the fluorindine group, but its constitution, like that of the previous dye, is unknown.

Dinitrophenylamidotoluylamine, $\mathrm{C_6H_3(NO_2)_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH_2}$

$$[\mathrm{NH} : (\mathrm{NO_2})_2 = 1 : 2 : 4;\ \mathrm{NH} : \mathrm{NH_2} = 1 : 2],$$

is prepared by the action of dinitrochlorobenzene on orthotoluylenediamine; it crystallises from alcohol in brownish-yellow needles, melts at 147°, and is insoluble in water, but readily dissolves in benzene or chloroform. The compound is soluble in acids, with a pale-yellow colour.

Dinitrophenylazimidotoluene,  $\mathrm{N}<\begin{smallmatrix}\mathrm{C_6H_3Me}\\ \mathrm{N}\text{——}\end{smallmatrix}>\mathrm{N{\cdot}C_6H_3(NO_2)_2}$, is prepared by the action of nitrous acid on the previous compound; it crystallises from alcohol in small, pale, brownish-yellow needles, melts at 186°, and is insoluble in ether, but readily dissolves in benzene, chloroform, or glacial acetic acid.

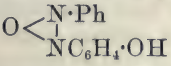
Dinitrophenyl-β-naphthylamine, $\mathrm{C_{10}H_7{\cdot}NH{\cdot}C_6H_3(NO_2)_2}$ $[\mathrm{NH} : (\mathrm{NO_2})_2 = 1 : 2 : 4]$, is prepared from dinitrochlorobenzene and β-naphthylamine; it is somewhat sparingly soluble in alcohol, from which it is deposited in brick-red crystals, and melts at 179°.

Dinitrophenyl-β-naphthol, $\mathrm{C_{10}H_7{\cdot}O{\cdot}C_6H_3(NO_2)_2}$ $[\mathrm{O} : (\mathrm{NO_2})_2 = 1 : 2 : 4]$, is obtained from β-naphthol as a pale-yellow, viscid liquid which solidifies after some time, and crystallises from alcohol in stellate groups of pale-yellow needles melting at 95°.

The corresponding diamido-derivatives are prepared by the reduction of these three nitro-compounds; *diamidophenylamidotoluylamine* and *diamidophenyl-β-naphthylamine* yield azo-derivatives on oxidation, but *diamidophenyl-β-naphthol* does not yield any colouring matter.

J. B. T.

Action of Phosphorus Pentachloride on Hydroxyazobenzene. By K. HEUMANN and R. PAGANINI (*Ber.*, **23**, 3550—3554).—The action of phosphorus pentachloride on hydroxyazobenzene was first examined in 1870 by Kekulé and Hidegh (*Ber.*, **3**, 235), who obtained a compound which they believed to be hydroxyazobenzene,



$$O<\begin{matrix}N\cdot Ph\\ |\\ NC_6H_4\cdot OH\end{matrix}$$

The reaction was also examined by Wallach and Belli, and Wallach and Kiepenheuer (Abstr., 1880, 556; 1882, 393), who also found the formula $C_{12}H_{10}N_2O_2$, and showed that the substance is reconverted by sodium in alcoholic solution into hydroxyazobenzene, but that it does not yield an acetyl compound, and is insoluble in alkalis. The last two properties are not in favour of the above constitutional formula, and the authors have therefore reinvestigated the reaction. They find that when equal parts of hydroxyazobenzene and phosphorus pentachloride are warmed on the water-bath until evolution of hydrogen chloride ceases, and the product no longer dissolves in alkali with a deep-yellow colour, a mixture of two compounds is obtained which may be separated by the difference in their solubilities in alcohol. The one agrees in all its properties with the so-called hydroxyazoxybenzene, and crystallises from acetone in golden-yellow plates melting at 148°. It was, however, found to contain phosphorus, the empirical formula being $C_{36}H_{27}N_6O_4P$, which agrees equally well with the figures for carbon, hydrogen, and nitrogen given by the investigators named above. Its ready conversion into hydroxyazobenzene is due, not to a reducing action, but to the alkali present, as zinc-dust and alcohol are without action on it. It is therefore *benzeneazophenyl phosphate*, $PO(O\cdot C_6H_4\cdot N\colon NPh)_3$, and may also be prepared by acting on the potassium salt of hydroxyazobenzene with phosphorus oxychloride.

The second product of the reaction crystallises in broad, orange-yellow needles, melts at 88°, and sublimes in golden plates. It is identical with the parachlorazobenzene prepared by Heumann and Mentha (Abstr., 1886, 874) from paramidoazobenzene. H. G. C.

Thiophenylhydrazine. By J. RUHL (*Ber.*, **23**, 3482—3483).—*Thiophenylhydrazine*, $S(C_6H_4\cdot NH\cdot NH_2)_2$, may be readily obtained from thioaniline by diazotising, adding sodium hydrogen sulphite, and reducing with zinc-dust. On the addition of concentrated hydrochloric acid, the *hydrochloride* separates out as a sparingly soluble salt, which is collected, pressed, dissolved in water, and treated with alkali, which precipitates the free base in small plates. The latter, after washing with cold water, is recrystallised from the hot liquid, and separates in yellowish, lustrous plates which, on drying, form a mass resembling paper. It melts at 115°, decomposes at 130°, is sparingly soluble in cold, more readily in hot water, easily in alcohol, and reduces Fehling's solution in the cold. Its *hydrochloride* and *sulphate* form white powders.

Thiophenylhydrazine readily combines with 2 mols. benzaldehyde, forming the crystalline hydrazone, $S(C_6H_4{\cdot}N_2H{:}CHPh)_2$; it also combines with phenylcarbamide. H. G. C.

Diamylphenylhydrazone. By S. Grimaldi (*Chem. Centr.*, 1890, ii, 553; from *L'Orosi*, 13, 190—193).—In manner similar to that used for the preparation of nonylmethylphenylhydrazone (Abstr., 1890, 1394), the author has now prepared its isomeride, *diamylphenylhydrazone*, from diamyl ketone, which was obtained by the dry distillation of calcium capronate. The ketone combines readily with phenylhydrazine, the elimination of water commencing at ordinary temperatures, and considerable development of heat occurring during the process. *Diamylphenylhydrazone*, $C(C_5H_{11})_2{:}N{\cdot}NHPh$, is an oily, slightly-red liquid, having a strong, agreeable odour, but burning taste. It is neutral, insoluble in water, soluble in ether, alcohol, chloroform, &c.; sp. gr. = 0·93896 at 0°. It remains fluid at −9·5°. J. W. L.

Isomeric Forms of Orthonitrophenylglyoxylic Hydrazone. By A. Krause (*Ber.*, 23, 3617—3622; compare Fehrlin, Abstr., 1890, 1117).—The hydrazone is converted into an isomeric form (m. p. 188—189°) by the action of aqueous potash in the cold; soda is, however, without action. Both compounds yield lead salts, from which, on treatment with sulphuric acid, the original substances are regenerated. Isatic hydrazone, together with a little aniline, is formed from each compound on reduction with stannous chloride.

By heating the hydrazone with sodium ethoxide and twice the molecular proportion of ethyl iodide in a sealed tube for three hours at 130—140°, the *ethyl salt* is obtained, crystallising from alcohol in yellow prisms melting at 126—128°. No diethyl derivative could be prepared.

When treated with hydrochloric acid, the hydrazone decomposes into ammonia, aniline, and resinous matters.

Metanitrophenylglyoxylic hydrazone is dissolved in alcohol and treated with aqueous potash; a sparingly soluble salt is formed which is allowed to remain for 24 hours; on the addition of hydrochloric acid, evolution of gas takes place, and a green, insoluble compound is obtained which melts at 284—285°.

The author considers that from these results the formulæ previously advanced for the two orthonitro-derivatives are no longer probable, and he suggests that the isomerism of the compounds may be of a stereometric nature, similar to that of many oximes, and explicable by the same hypotheses. J. B. T.

Phenacyl Sulphide. By J. Tafel and A. Mauritz (*Ber.*, 23, 3474—3475).—In a paper recently published by Delisle (*Annalen*, 260, 250), the latter has described acetonyl phenyl sulphide, and has announced his intention of preparing other ketonic sulphides. The authors have already obtained *phenacyl sulphide*, $S(CH_2{\cdot}COPh)_2$, and in view of the above paper of Delisle, now publish the results of their investigation.

Phenacyl sulphide is readily prepared by dissolving 100 parts of bromacetophenone in 400 parts of alcohol, and adding a solution of 12 parts of sodium in 400 parts of alcohol saturated with hydrogen sulphide, cooling well during the addition, and subsequently heating for a short time on the water-bath. It crystallises from alcohol in compact, colourless prisms, melts at 77°, is very slightly soluble in hot water, readily in alcohol, acetic acid, chloroform, and benzene, and also dissolves in cold concentrated sulphuric acid with a yellow colour. It is coloured yellow by boiling alkalis, and reduces Fehling's solution without deposition of cupric sulphide. On treatment with an alkaline solution of hydroxylamine, it yields the *dioxime*,

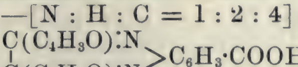
$$S(CH_2\cdot CPh{:}NOH)_2,$$

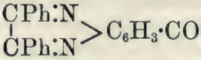
which is recrystallised from acetic acid. It melts at 151°, and is sparingly soluble in water, light petroleum, and benzene, readily in alcohol, ether, and acetic acid. The *dihydrazone*,

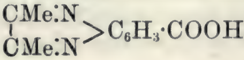
$$S(CH_2\cdot CPh{:}N_2HPh)_2,$$

obtained by heating the sulphide with phenylhydrazine at 100°, crystallises from alcohol in slender, colourless needles which become yellow in the air; it melts at 146—147°. It is readily soluble in benzene and chloroform, almost insoluble in water and dilute acids, but dissolves in cold concentrated sulphuric acid with a yellowish-green colour.

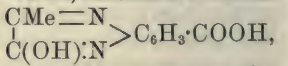
When bromacetophenone is boiled with alcoholic soda, it yields a crystalline compound of as yet unascertained constitution, which seems to have the formula $C_{16}H_{13}O_2Br$. H. G. C.

Metaparadiamidobenzoic Acid. By A. ZEHRA (*Ber.*, **23**, 3625—3635).—[N : H : C = 1 : 2 : 4] *Difuranylquinoxalinemetacarboxylic acid*,  $\begin{array}{l}C(C_4H_3O){:}N\\ |\\ C(C_4H_3O){:}N\end{array}\!>C_6H_3\cdot COOH$, is prepared by the action of furile on metaparadiamidobenzoic acid in glacial acetic acid solution; it crystallises from alcohol in pale-yellow needles, softens at 235°, and melts at 245°. The compound is insoluble in benzene, but dissolves in dilute ammonia or alkaline carbonates; with hydrochloric acid, it yields a yellowish-red colour, whilst the sulphuric acid solution is cherry-red, and the original substance is precipitated unchanged on the addition of water. The *barium salt*, $(C_{17}H_9N_2O_4)_2Ba$, crystallises in pale-yellow needles.

Diphenylquinoxalinemetacarboxylic acid,  $\begin{array}{l}CPh{:}N\\ |\\ CPh{:}N\end{array}\!>C_6H_3\cdot COOH$, prepared from diamidobenzoic acid and benzile, crystallises from glacial acetic acid or alcohol in yellowish plates or needles, softens at 280°, and melts at 288°. It is very sparingly soluble in organic media, but dissolves in alkaline carbonates and hydrochloric acid. The *barium salt*, $(C_{21}H_{13}N_2O_2)_2Ba + 3H_2O$, crystallises from dilute alcohol in small, white needles. The *ethyl* salt is deposited from alcohol in white needles, melts at 151°, and is insoluble in ammonia.

Dimethylquinoxalinemetacarboxylic acid,  $\begin{array}{l}CMe{:}N\\ |\\ CMe{:}N\end{array}\!>C_6H_3\cdot COOH$, is

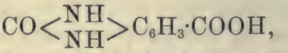
prepared from diamidobenzoic acid and diacetyl; it crystallises from alcohol in small, white needles, softens at 250°, and melts at 257—260° with decomposition. It is readily soluble in alkaline carbonates and hydrochloric acid, but more sparingly in benzene or ether. The *silver salt*, $C_{11}H_9N_2O_2Ag$, is obtained in small, white, insoluble needles.

Methylhydroxyquinoxalinecarboxylic acid,  $\begin{matrix}CMe{=}N\\ \vert\\ C(OH){:}N\end{matrix}{>}C_6H_3{\cdot}COOH$, prepared from diamidobenzoic acid and pyruvic acid, resembles the previous compound, and crystallises in white needles which blacken at 330° without melting. The *barium salt*, $(C_{10}H_7N_2O_3)_2Ba + 3H_2O$, is deposited in pale-yellow needles.

Methyl phenylenedicarboxymetaparadicarbamate,

$$C_6H_3(NH{\cdot}COOMe)_2{\cdot}COOH,$$

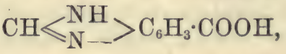
is obtained from diamidobenzoic acid and methyl chloroformate; it crystallises in lustrous needles, softens at 300° and melts at 350° with gas evolution; it is insoluble in water, but dissolves in alkaline carbonates. The *silver salt* is gelatinous.

Carbamidometaphenylcarboxylic acid,  $CO{<}\begin{matrix}NH\\NH\end{matrix}{>}C_6H_3{\cdot}COOH$, prepared from diamidobenzoic acid and carbonyl chloride, is deposited in small needles or plates which are scarcely altered at 360°; it is very sparingly soluble except in alkaline carbonates.

Diacetylmetaparadiamidobenzoic acid, $C_6H_3(NHAc)_2{\cdot}COOH$, crystallises from alcohol in small, white needles, melts at 218° with evolution of gas, and is sparingly soluble in dilute hydrochloric acid.

Formylparamidobenzoic acid, $COOH{\cdot}C_6H_4{\cdot}NH{\cdot}COH$ [N : C = 1 : 4], is prepared by dissolving paramidobenzoic acid in concentrated formic acid; it crystallises from alcohol in short, white needles and melts at 268° with decomposition. *Metanitroformylparamidobenzoic acid* is formed by the action of fuming nitric acid on the previous compound; it crystallises from alcohol in pale yellow needles, and melts at 221° with evolution of gas.

Methenylamidinephenylenemetacarboxylic acid,



$$CH{\lessgtr}\begin{matrix}NH\\N\text{--}\end{matrix}{>}C_6H_3{\cdot}COOH,$$

is prepared by the reduction of the nitro-compound, and crystallises from dilute formic acid in white needles which decompose at 325° without melting. The *hydrochloride*, *sulphate*, and *nitrate* are crystalline.

J. B. T.

Substitution of the Anilido-group for Halogen Atoms in the Benzene Nucleus. By M. Schöpff (*Ber.*, **23**, 3440—3445).—The behaviour of aniline towards parabromometanitrobenzoic acid has already been described (compare Abstr., 1890, 374). The author finds that a similar reaction takes place between aniline and orthobromometanitrobenzoic acid and the corresponding ortho- and paranitriles and amides and the sodium salts of the acids.

Metanitro-orthanilidobenzoic acid, $NHPh{\cdot}C_6H_3(NO_2){\cdot}COOH$, prepared by the action of aniline on orthobromometanitrobenzoic acid, is obtained in small, straw-coloured needles, by precipitating its alcoholic solution with water; it melts at 247—248°. The anhydrous sodium salt is obtained as a brick-red compound by adding the theoretical quantity of sodium to a solution of the acid in absolute alcohol; it absorbs moisture from the air, and then crystallises in yellow needles containing 2 mols. H_2O, which are lost over sulphuric acid. The barium, calcium, lead, copper, silver, and mercury salts were also prepared. The *ethyl* salt of the above acid crystallises from alcohol in yellow plates, and melts at 121°.

Metanitroparanilidobenzonitrile, $NHPh{\cdot}C_6H_3(NO_2){\cdot}CN$, is obtained by carefully heating the bromonitrile with aniline for a short time; it crystallises from alcohol in short, brick-red needles or plates and from hot water in needles, melts at 126°, and is easily soluble in alcohol, acetone, chloroform, and benzene, less soluble in light petroleum. Nitranilidobenzanilide and nitranilidobenzamide are formed in this reaction if the heating is prolonged, as the hydrogen bromide liberated in the formation of the anilidonitrile hydrolyses it to amide. These two compounds are easily separated, as the former is only slightly, the latter easily, soluble in hot alcohol. Metanitroparanilidobenzamide crystallises in yellow needles, melts at 187°, and by the further action of aniline is converted into metanitroparanilidobenzanilide.

Metanitro-orthanilidobenzonitrile, $NHPh{\cdot}C_6H_3(NO_2){\cdot}CN$, is sparingly soluble in hot water, but easily soluble in alcohol; by precipitation with water, it is obtained in lemon-yellow needles which melt at 170°. Unlike the para-compound, it is not hydrolysed by prolonged heating with the hydrogen bromide formed in the reaction.

E. C. R.

Derivatives of Parabromometanitrobenzoic Acid. By A. Grohmann (*Ber.*, **23**, 3445—3450).—*Parabromometanitrobenzoic chloride*, $NO_2{\cdot}C_6H_3Br{\cdot}COCl$, obtained by the action of phosphorus pentachloride on parabromometanitrobenzoic acid, forms yellowish-white needles, melts at 51—53°, and is soluble in benzene, acetone, and chloroform, slightly soluble in light petroleum. When this compound is gently warmed with aniline, parabromometanitrobenzanilide is formed; at a higher temperature and in presence of excess of aniline, metanitroparanilidobenzanilide is formed. *Parabromometanitrobenzanilide* crystallises from alcohol in beautiful, orange-yellow crystals belonging to the monosymmetric system, and melts at 156°. It is soluble in alcohol, ether, benzene, carbon bisulphide, chloroform, and acetone, sparingly soluble in light petroleum, and insoluble in water. *Metanitroparanilidobenzanilide* forms leafy crystals, melts at 216°, and is soluble in alcohol, benzene, chloroform, acetone, and acetic acid, but insoluble in light petroleum.

Parabromometanitrobenzamide is best prepared by warming the chloride with ammonium carbonate. It crystallises from alcohol in colourless needles, melts at 156° (compare preceding abstract) and is soluble in alcohol, ether, and acetone, insoluble in water, light petroleum, chloroform, benzene, and carbon bisulphide. *Metanitroparamidobenzamide*, obtained by heating the bromamide with alcoholic ammonia at 180°, crystallises in lemon-yellow needles, melts at 227°, and is soluble in acetone, acetic acid, sparingly in alcohol, and insoluble in water, benzene, light petroleum, and chloroform.

By the action of ammonia or aniline on ethyl parabromometanitrobenzoate, the halogen is displaced by the amido- or anilido-group; the ethoxy-group remains unaltered.

Ethyl metanitroparamidobenzoate melts at 145° and is soluble in alcohol, benzene, chloroform, acetone, ether, acetic acid, and aniline, insoluble in light petroleum. Ethyl metanitroparanilidobenzoate melts at 123° (compare Abstr., 1890, 374). E. C. R.

Toluidonitrobenzoic Acid and Naphthylamidonitrobenzoic Acid. By E. HEIDENSLEBEN (*Ber.*, **23**, 3451—3458).—*Metanitropara-(ortho)toluidobenzoic acid*, $C_6H_4Me\cdot NH\cdot C_6H_3(NO_2)\cdot COOH$, is prepared by heating equal weights of orthotoluidine, bromonitrobenzoic acid, and glycerol in a reflux apparatus until the liquid, on cooling, solidifies to a brown mass. It crystallises from dilute alcohol in bright-brown needles, melts at 210—211°, and is easily soluble in alcohol, chloroform, benzene, acetic acid, and ether. The sodium salt, prepared by adding sodium to the alcoholic solution of the acid, crystallises in beautiful, dark-red needles. The *ethyl* salt forms bright-yellow plates, melts at 106°, and is easily soluble in alcohol, ether, chloroform and benzene.

Metamidopara(ortho)toluidobenzoic acid,

$$C_6H_4Me\cdot NH\cdot C_6H_3(NH_2)\cdot COOH,$$

is prepared by heating the nitro-acid with alcoholic ammonium sulphide at 120°. It crystallises from dilute alcohol in white needles, melts at 167°, rapidly colours in the air, and dissolves in alcohol, acetone, and benzene. The ethyl salt is prepared by reducing the corresponding nitro-compound with alcoholic ammonium sulphide; it melts at 115°, and is easily soluble in alcohol, ether, and chloroform, slightly soluble in benzene.

Metanitropara(para)toluidobenzoic acid,

$$C_6H_4Me\cdot NH\cdot C_6H_3(NO_2)\cdot COOH,$$

has already been described by M. Schöpff. The sodium salt forms beautiful, dark-red needles. The *ethyl* salt crystallises in beautiful dark-yellow shining plates, melts at 115°, and is easily soluble in alcohol, ether, and benzene.

Metamidopara(para)toluidobenzoic acid,

$$C_6H_4Me\cdot NH\cdot C_6H_3(NH_2)\cdot COOH,$$

crystallises from dilute alcohol in bright yellow needles, melts at 185·5°, and is easily soluble in alcohol and acetone, insoluble in water. The *ethyl* salt crystallises in colourless needles, which turn blue on exposure to air, melts at 145°, and dissolves easily in alcohol, ether, and chloroform, sparingly in benzene.

Azimidopara(para)toluidobenzoic acid is obtained by acting on metamidopara(para)toluidobenzoic acid (2 grams) dissolved in absolute alcohol (20 c.c.), with amyl nitrite (4 c.c.), and a few drops of concentrated hydrochloric acid. It crystallises from alcohol in beautiful, rose-red needles, and melts at 271°. The nitrazimido-compound is obtained by dissolving the azimido-compound in fuming nitric acid and precipitating with water. It forms a yellowish-white, non-crystalline powder, and melts at 253°.

Orthamidophenylpara(para)tolylamine, $C_6H_4Me{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$, is obtained by distilling the amido-acid under diminished pressure, and may be purified by precipitation from its aqueous solution with ammonia. It crystallises from water in colourless plates which redden on exposure to air, melts at 74°, and is easily soluble in alcohol, ether, chloroform, and benzene. When dissolved in hydrochloric acid, oxidation takes place, and the solution becomes red.

Metanitropara-β-naphthylamidobenzoic acid,

$$C_{10}H_7{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}COOH,$$

is best prepared by heating a mixture of parabromometanitrobenzoic acid (1 part), β-naphthylamine (2 parts), and glycerol (3 parts) to boiling in a reflux apparatus. The compound, when pure, is brick-red, and is soluble in alcohol, acetone, and acetic acid, less soluble in benzene and chloroform, and insoluble in water. The sodium salt is a red, amorphous powder soluble in water. The *ethyl* salt crystallises from ether in beautiful, bright-yellow needles, melts at 127·5, and is soluble in alcohol, acetone, acetic acid, and chloroform.

Metanitropara-α-naphthylamidobenzoic acid is prepared in the same way as the β-acid. It forms a red-brown, amorphous powder, and is easily soluble in dilute alcohol, &c., and somewhat soluble in hot water. The *sodium* salt forms a dark-red, amorphous powder. The *ethyl* salt crystallises in beautiful, red-brown plates, melts at 109°, and is easily soluble in alcohol, benzene, acetic acid, and chloroform.

Metamidopara-α-naphthylamidobenzoic acid,

$$C_{10}H_7{\cdot}NH{\cdot}C_6H_3(NH_2){\cdot}COOH,$$

prepared by reducing the nitro-acid with alcoholic ammonium sulphide, crystallises in white needles, which become red on exposure to air, decomposes at 90°, and is easily soluble in alcohol, benzene, ether, and chloroform, insoluble in water. E. C. R.

Nitration of Hydroxybenzoic Acids by Nitrous Acid. By A. Deninger (*J. pr. Chem.* [2], **42**, 550—553).—When salicylic acid is nitrated with nitric acid, the nitro-acid of m. p. 228° is the chief product, that of m. p. 144° being obtained in small quantity only. By the following methods, each can be obtained practically free from the other.

Asymmetrical metanitrosalicylic acid [m. p. 228°; $COOH : OH : NO_2 = 1 : 2 : 5$] is obtained by mixing salicylic acid (100 grams) and sodium nitrite (130 grams) with water (150 grams), and slowly adding 1·2 litres of sulphuric acid (sp. gr. 1·52), so that the temperature may not rise above 15°, vigorous stirring being kept up during the process. After some four hours, the liquid is warmed to 50°, and after several hours more, the solid is filtered and recrystallised from water.

Consecutive metanitrosalicylic acid (m. p. 144°) is obtained by mixing salicylic acid (100 grams) and sodium nitrite (170 grams), with water (150 grams), and adding 1 litre of sulphuric acid (sp. gr. 1·52) at 60° all at once, so that the temperature may rise quickly, as otherwise much of the acid of m. p. 228° will be formed. The solution of the solid mass in water must be heated with animal charcoal for some time to eliminate orthonitrophenol.

Metanitroparahydroxybenzoic acid (m. p. 185°) is obtained by mixing parahydroxybenzoic acid (100 grams) and sodium nitrite (200 grams) with water (200 grams), adding 1 litre of sulphuric acid (sp. gr. 1·52) at 40°, and heating for a long time on the water-bath. When sodium nitrite and cold sulphuric acid are added to the parahydroxy-acid, no nitro-acid is formed; but, if the nitrite and sulphuric acid are mixed first, and the hydroxybenzoic acid then added, the yield of nitro-acid is abundant; this shows that the formation of nitrosylsulphuric acid is necessary, a conclusion proved by substituting this acid for the mixed sodium nitrite and sulphuric acid with good results. Phenol cannot be nitrated like this. A. G. B.

Ortho- and Meta-cresotic Acid. By R. NIETZKI and F. RUPPERT (*Ber.*, **23**, 3476—3480).—Orthocresotic acid unites with diazobenzene chloride in the usual manner, forming an azo-dye, which is readily converted by reduction with stannous chloride into *amidorthocresotic acid.* On the addition of concentrated hydrochloric acid, the *hydrochloride* separates as a precipitate which is readily soluble in water, although but sparingly in hydrochloric acid, and may be readily purified by dissolving in water and precipitating with acid. On dissolving it in aqueous sodium carbonate and saturating with acetic acid, the free amido-acid is obtained in small, colourless plates, which are very sparingly soluble in the common solvents, and melt with decomposition above 300°. According to Jacobsen, orthocresotic acid has the constitution [OH : Me : COOH = 1 : 2 : 6], and as the azo-group almost invariably replaces the hydrogen atom in the para-position to the hydroxyl group, it is probable that the amido-group in the above acid occupies the position 4.

When amidorthocresotic acid is treated with acetic anhydride and sodium acetate, it yields a *diacetyl* compound, which is very soluble and difficult to purify. On warming it with dilute alkali, the acetyl group in combination with the hydroxyl is eliminated, and on the addition of an acid, the *monacetyl* derivative is precipitated in small, colourless needles melting at 275°. On treating the amido-acid with nitrous acid, a very stable diazo-compound is formed, which may be recrystallised from hot water; on reduction, it yields a hydrazine derivative. On distilling the acid with quicklime or sodium carbonate, it yields paramidorthocresol, thus confirming the above assumption with regard to the position of the amido-group.

When acetylamidocresotic acid is nitrated in acetic acid solution, the carboxyl group is eliminated, and its place taken by the nitro-group. The *acetylamidonitrocresol* thus formed crystallises from alcohol in thick, yellow needles which melt at 217°; on boiling with dilute sulphuric acid, it yields the corresponding amidonitrocresol. This separates from alcoholic solution in long, brownish-red needles melting at 118°, and forms beautiful, red, crystalline salts with alkalis. On treatment with nitrous acid, it yields a diazo-compound, crystallising in yellow needles, which may be dried at 70—80°, but explode at a higher temperature. It is almost unaltered by boiling alcohol, but the diazo-group may be removed if a moderate quantity of alkali be added to the boiling solution. The nitrocresol thus formed is identical with the one obtained by Hofmann and v. Miller, which has the constitution [$Me : OH : NO_2 = 1 : 2 : 3$], showing that the nitro-group has, in reality, taken the position previously occupied by the carboxyl.

Metacresotic acid was treated in exactly the same manner as the ortho-compound. The *amidometacresotic acid* obtained from it forms small, colourless plates which melt at 265°. From analogy, the most probable constitution is [$OH : Me : NH_2 : COOH = 1:3:4:6$], and this is proved by the fact that, on distillation with sodium carbonate, it yields paramidometacresol, which is converted by oxidation into toluquinone. On treatment with nitrous acid, amidometacresotic acid yields a diazo-compound similar to that obtained from the ortho-compound; this also yields a hydrazine on reduction. The *diacetyl* and *monacetyl* compounds are also obtained in a similar manner. The latter may also be nitrated with elimination of the carboxyl group, but in this case a dinitro-compound is obtained, which forms thick, yellow crystals melting at 225°, and has acid properties, forming a potassium salt which crystallises in beautiful, red needles. On warming with dilute sulphuric acid, it yields *amidodinitrocresol*, which crystallises from alcohol in ruby-red needles melting at 160°, and has both acid and basic properties. On heating with acetic anhydride, it yields a *diacetyl* derivative melting at 175°.

When amidodinitrocresol is treated with nitrous acid, it yields a very explosive diazo-compound, crystallising in yellow plates. The diazo-group may be removed by boiling with alcohol in weak alkaline solution; the dinitrocresol thus obtained crystallises in orange-red needles melting at 99°. The constitution of the latter can only be represented by one of the following formulæ, if it be assumed that one nitro-group takes the place of the carboxyl in the amido-acid,

$$\text{I. } [OH : NO_2 : Me : NO_2 = 1 : 2 : 3 : 6],$$
$$\text{II. } [OH : Me : (NO_2)_2 = 1 : 3 : 5 : 6].$$

Of these the former is the more probable, as compounds in which the nitro-groups occupy the adjacent position are usually unstable; moreover, on reduction, it yields a diamido-compound, which does not form an azine or quinoxaline on treatment with orthodiketones.

H. G. C.

Saligeninoxyacetic Acid. By P. Biginelli (*Chem. Centr.*, 1890, ii, 623—624; from *Ann. Chim. Farm.*, **12**, 69—72).—*Saligeninoxyacetic acid*, $OH·CH_2·C_6H_4·O·CH_2·COOH$, is prepared by warming saligenin with chloracetic acid in presence of sodium hydroxide. The mixture is first warmed on the water-bath, and finally over the flame directly. The mass is then dissolved in a little water, and the acid liberated by the addition of sulphuric acid. The acid may be recrystallised from water, and is thus obtained in white, lustrous plates melting at 120°. The solutions of the sodium and potassium salts are precipitated by lead acetate, calcium chloride, and silver nitrate, but not by barium chloride. The lead and calcium salts are powdery; the silver salt has the formula $C_9H_9O_4Ag + 2H_2O$. It loses 1 mol. H_2O readily, but retains the second molecule somewhat persistently. By treating the silver salt with methyl iodide, an ethereal salt of the formula $C_{19}H_{20}O_7$ is obtained, which probably has the constitutional formula $OH\cdot CH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COO\cdot CH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot COOMe$.

If saligeninoxyacetic acid is heated in a current of dry air at 100—108°, it loses 1 mol. H_2O, and becomes converted into a caramel-like substance of the formula $C_9H_8O_3$, and melting at 140°. It is insoluble in all ordinary menstrua, and dissolves only in soda or potash. J. W. L.

Thionylamines, a New Class of Compounds containing Sulphur. By A. Michaelis and R. Herz (*Ber.*, **23**, 3480—3482).—It has already been shown by Michaelis (Abstr., 1890, 617) that thionyl chloride readily acts on primary and secondary asymmetrical hydrazines forming compounds in which the hydrogen atoms of the NH_2 group are displaced by the SO_2 group. The authors find that the same reaction takes place even more readily with the simple amido-compounds. The action of this reagent on aniline has also been examined by Schiff (*Annalen*, **102**, 111) and Böttinger (Abstr., 1878, 863). The authors proceeded in a similar manner to the last-named, dissolving 20 grams of aniline in double its volume of dry benzene and adding 20 grams of thionyl chloride also diluted with benzene, when separation of a solid substance and development of heat takes place. The viscid mass is then heated in a reflux apparatus, when a further reaction takes place, and the contents of the flask become thin. After cooling, the precipitated aniline hydrochloride is filtered off, and the clear liquid distilled. As soon as the benzene has passed over, the thermometer rises to 198—200° and a yellow liquid condenses, which after redistillation is quite pure, and as shown by its analysis, consists of *thionylaniline*, $SO\colon NPh$. This boils at 200°, has an aromatic and somewhat pungent odour, and is slowly decomposed by water and dilute acids, and quickly by alkalis with formation of aniline and an alkaline sulphate.

Thionylparatoluidine, $C_7H_7\cdot N\colon SO$, is prepared in a similar manner; it is a yellow liquid which has an aromatic odour, boils at 224°, and solidifies in a freezing mixture to well-developed, yellow crystals melting at 7°.

The reaction appears to be quite general, the thionyl group playing the same rôle with primary amines as the nitroso-group does with secondary amines. H. G. C.

Metethoxyphenylsulphonic Acid. By A. Delisle and G. Lagai (*Ber.*, **23**, 3392—3394).—*Potassium metethoxyphenylsulphonate*,

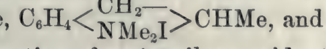
$$OEt\cdot C_6H_4\cdot SO_3K + H_2O,$$

is deposited from water in hard, octahedral crystals, and from dilute alcohol in long, flat, lustrous needles. The *barium salt*, $C_8H_9SO_4Ba + 4H_2O$, crystallises in needles; the *calcium salt*, $(C_8H_9SO_4)_2Ca + 3H_2O$, is deposited in thin, colourless plates. The free *acid* crystallises with difficulty, and is readily soluble in water or alcohol. The *sulphochloride* crystallises from ether in hard, pale-yellow needles, and melts at 38°. The *sulphonamide* crystallises from water in long, white needles and melts at 131°. The *hydrosulphide*, $OEt\cdot C_6H_4\cdot SH$, is prepared by the reduction of the sulphochloride, boils at 238—239°, and on warming with sulphuric acid gives a yellow coloration which changes successively to red, green, and blue. J. B. T.

Synthesis of Indigo and Allied Dyes. By K. HEUMANN (*Ber.*, **28**, 3431—3435).—Phenylglycocineorthocarboxylic acid is prepared by heating anthranilic acid (63 parts) with chloracetic acid (47 parts) and water (500 parts) for two hours in a reflux apparatus. It crystallises from hot water as a yellowish, granular mass, and melts at about 200° with decomposition. It is only slightly soluble in cold water. The alcoholic solution shows a blue fluorescence. The preparation of indigotin from this compound is best carried out as follows:—Phenylglycocineorthocarboxylic acid (1 part) is fused with potash (3 parts) and water (1 part), with constant stirring, and the mixture heated at 180—200° as long as it deepens in colour. The melt is treated with water, oxidised with a current of air or with ferric chloride and hydrochloric acid, and the precipitated indigo collected and washed. The temperature of the reaction is 60—80° lower than is the case when phenylglycocine is employed (compare this vol., p. 75). E. C. R.

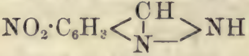
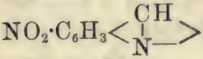
Synthesis of Indigo from Phenylglycocine. By L. LEDERER (*J. pr. Chem.* [2], **42**, 565—567).—The author combats Heumann's claim for priority in this matter (this vol., pp. 75, 206). With regard to Heumann's criticism that the indigo cannot actually exist in the melt, the author points out that when indigotin is melted with sodium hydroxide in a test-tube, the melt first becomes yellow and then orange-red, subsequently again giving indigo-blue when treated with dilute sulphuric acid; this behaviour is exactly similar to that of phenylglycocine and sodium hydroxide when melted together.

A. G. B.

Action of Methyl Iodide on Hydro-α-methylindole. By C. ZATTI and A. FERRATINI (*Chem. Centr.*, 1890, ii, 554; from *Rend. Acad. Lincei*, **6**, i, 463—466).—By boiling hydro-α-methylindole (1 part) with methyl iodide (3 parts) for 20 minutes in a reflux apparatus, an oil is formed which is insoluble in the excess of iodide. After distilling off the methyl iodide, the oily substance solidifies, and may be recrystallised from alcohol. It is of a slightly red colour, smells of indole, and melts at 200—202°. It is the iodide of an ammonium base,  $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2—}{NMe_2I}}{>}CHMe$, and dissolves in water and alcohol. By the action of moist silver oxide, the *free base* may be obtained. The latter is crystalline, and absorbs moisture and carbonic anhydride from the air. By agitating the iodide with freshly precipitated silver chloride, the *chloride* is formed, which is also hygroscopic. From it, the aurochloride and platinochloride may be prepared.

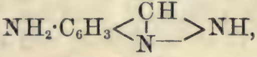
J. W. L.

Indazole Derivatives. By O. N. Witt, E. Nölting, and E. Grandmougin (*Ber.*, **23**, 3635—3644).—The conversion of nitrotoluidine [$Me : NH_2 : NO_2 = 1 : 2 : 4$] into the corresponding phenol by means of the diazo-reaction is only complete under certain special conditions, for example, by the addition of sodium nitrite to the base dissolved in hot hydrochloric acid; in ordinary circumstances, more or less nitroindazole is formed, probably on account of the close proximity of the methyl and diazo-groups.

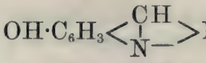
Nitroindazole,  $NO_2\cdot C_6H_3<\overset{CH}{\underset{N—}{|}}>NH$ [$CH : NH : NO_2 = 1 : 2 : 4$], is prepared by dissolving nitrotoluidine (30 grams) in 60 grams of concentrated sulphuric acid, diluted with 1 litre of water; the solution is cooled, mixed with 14 grams of sodium nitrite dissolved in 200 c.c. of water, and slowly warmed on the water-bath; it is finally boiled for a short time, and, on cooling, a mixture of nitroindazole and nitrocresol is deposited; this may be separated by repeated crystallisation from water or xylene; the pure product is obtained in white, lustrous needles which melt at 181°, and, in small quantities, may be volatilised without decomposition. The *sodium salt* crystallises in yellow needles. The *silver salt* is also yellow. The *methyl ether*,  $NO_2\cdot C_6H_3<\overset{CH}{\underset{N—}{|}}>NMe$, is obtained by the action of methyl iodide and alcoholic potash on nitroindazole or the mixture of this and the cresol; it crystallises from benzene in pale-yellow, flat needles, melts at 159°, is insoluble in light petroleum, and yields azoxy-derivatives on prolonged heating with alcoholic potash. The corresponding derivative of nitro-orthocresol crystallises from light petroleum in colourless needles melting at 74°. *Acetylnitroindazole* crystallises from alcohol in lustrous needles, melts at 139—140°, and sublimes without decomposition.

By the action of aqueous bromine on nitroindazole, a *monobromo*-derivative is formed, which is deposited from benzene in small, yellow prisms, and from alcohol in small needles, which melt at 229°. The *sodium salt* crystallises in red needles.

No satisfactory results were obtained by the oxidation of nitroindazole.

Nitroindazole may be reduced by the action of stannous chloride in acid solution; it is, however preferable to employ ammonium sulphide. *Amidoindazole*,  $NH_2\cdot C_6H_3<\overset{CH}{\underset{N—}{|}}>NH$, crystallises from water in white plates or needles; the former contain water of crystallisation, whilst the latter are anhydrous and melt at 210°. The *hydrochloride* is deposited from alcoholic solution in white needles, decomposes at 230° without melting, and is readily soluble.

By the action of sodium nitrite on a salt of amidoindazole, *hydroxy-*

indazole,  $\mathrm{OH{\cdot}C_6H_3}<\overset{\mathrm{CH}}{\underset{\mathrm{N}-}{|}}>\mathrm{NH}$, is obtained; it is deposited from water in colourless crystals, melts at 215—216° (? 265—266°), and sublimes without decomposition. Indazole is produced by elimination of the amido-group from amidoindazole, and is found to be identical with a specimen prepared according to the method of E. Fischer and Kuzel. No indazole could be obtained from orthotoluidine by the method described above. J. B. T.

Derivatives of Benzidinemetasulphonic Acid. By A. Zehra (*Ber.*, **23**, 3459—3464).—*Sodium diacetylbenzidinemetasulphonate*, $\mathrm{NHAc{\cdot}C_6H_4{\cdot}C_6H_3(NHAc){\cdot}SO_3Na}$, is prepared by heating sodium benzidinesulphonate with somewhat more than an equal weight of acetic anhydride. Unlike most alkali salts of acetamidosulphonic acids, it is sparingly soluble in cold water, but easily soluble in hot water, from which it crystallises in beautiful, long, colourless needles.

Metadinitrodiacetylbenzidinemetasulphonic acid,

$$\mathrm{NO_2{\cdot}C_6H_3(NHAc){\cdot}C_6H_2(NHAc)(NO_2){\cdot}SO_3H},$$

obtained by treating a solution of the above compound in concentrated sulphuric acid, cooled to +5°, with a mixture of concentrated nitric and sulphuric acids, has an orange-yellow colour, and is extremely soluble in water and alcohol. The *potassium* salt crystallises from hot water in yellow needles. By heating with dilute sulphuric acid (1 : 2), the acetyl groups are eliminated and *metadinitrobenzidinemetasulphonic acid*,

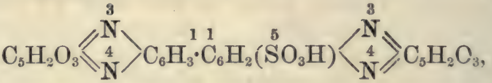
$$\mathrm{NO_2{\cdot}C_6H_3(NH_2){\cdot}C_6H_2(NH_2)(NO_2){\cdot}SO_3H},$$

is obtained as a dark-red, granular mass, very slightly soluble in both hot and cold water, but somewhat soluble in dilute mineral acids. The *potassium* salt crystallises in bright-red needles, and is only slightly soluble in hot and cold water; the *ammonium* and *sodium* salts show the same behaviour. The tetrazo-compound yields with β-naphthol a blue-black dye of coppery lustre, which does not dye cotton, and dyes wool in an acetic acid bath a garnet-red; with β-naphtholdisulphonic acid R., it gives a beautiful reddish-violet, and with β-naphtholdisulphonic acid G., a violet-black dye.

Metadiamidobenzidinemetasulphonic acid,

$$\mathrm{C_6H_3(NH_2)_2{\cdot}C_6H_2(NH_2)_2{\cdot}SO_3H},$$

is obtained by reducing the nitro-compound with tin and hydrochloric acid. The hydrochloride is extremely stable, and is easily soluble in hot water, slightly so in cold water. Sodium nitrate, when added to the acid solution, causes the precipitation of fine, yellow flocks, consisting probably of the azimide, but owing to the small quantity it could not be examined. Ferric chloride instantly darkens the solution, and precipitates a black compound. Platinic chloride does not form a double salt, but acts as an oxidising agent. The picrate crystallises in bright-yellow needles, and is sparingly soluble in alcohol and water. When a hot acid solution of the diamine is treated with the potassium salt of croconic acid, the azine,



$$C_5H_2O_3\left<\begin{matrix}\overset{3}{N}\\ \underset{4}{N}\end{matrix}\right>\overset{1}{C_6H_3}\cdot\overset{1}{C_6H_2}(\overset{5}{SO_3H})\left<\begin{matrix}\overset{3}{N}\\ \underset{4}{N}\end{matrix}\right>C_5H_2O_3,$$

is formed; this when dry has a black colour and green metallic lustre, and is very slightly soluble in water, but more soluble in dilute alkali, from which the *potassium* salt is precipitated in black, microcrystalline needles on the addition of concentrated potash. An aqueous solution of the azine is completely decolorised by barium chloride, and a heavy, black compound separates. E. C. R.

Fluorene Hydrides. By P. A. Guye (*Bull. Soc. Chim.*, [3], **4**. 266—268; compare Abstr., 1889, 720).—Fluorene (3·6 grams), phosphorus (3 grams), and hydriodic acid, sp. gr. 1·7 (9 grams), were heated in sealed tubes at 250—260° for 6—7 hours, and the liquid resulting from the extraction of the product with ether was fractionated over sodium. Two hydrides were obtained, a decahydride, $C_{13}H_{20}$, which boils at 254—256°, under a pressure of 727 mm., and which is still liquid at $-15°$, but crystallises above $-73°$, and is oxidised on contact with air, and an octohydride, $C_{13}H_{18}$, boiling at 272—275°, having properties similar to the former. Both these hydrides are soluble in ether and benzene, and have an odour like that of diphenylmethane. In addition to these hydrides, a sample of fluorene containing traces of phenanthrene yielded phenanthrene octohydride, boiling below 300°. T. G. N.

Oximes of Haloïd Benzophenones. By R. Demuth and M. Dittrich (*Ber.*, **23**, 3609—3617).—Parachlorobenzophenone, prepared from chlorobenzoic chloride and benzene, when acted on by hydroxylamine and excess of alkali in the cold, yields two oximes which may be separated by fractional crystallisation from alcohol; the one melts at 155—156° instead of 149°, as previously stated by Beckmann and Wegerhoff (Abstr., 1889, 1066), and is termed the α-oxime. The second, or β-, and more soluble modification, is deposited from dilute alcohol in square prisms melting at 95°. No other oxime could be isolated. Both compounds dissolve completely, although with some difficulty, in aqueous alkalis. The β-oxime is converted into the α-modification by heating for about three hours on the water-bath, but no change occurs on boiling with alcohol. Both compounds yield chlorobenzophenone when heated with hydrochloric acid for eight hours at 100°.

α-Acetylparachlorobenzophenone crystallises from alcohol in rhombohedra, and melts at 147—148°. The *β-acetyl* derivative is readily soluble in alcohol, from which it is deposited in long, slender needles, and melts at 105—106°. The hydroximes are regenerated from both compounds by the action of alcoholic potash.

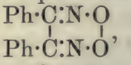
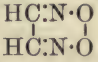
α-Parachlorobenzophenone benzyl ether is obtained by treating the hydroxime with benzyl chloride and sodium ethoxide, and crystallises from alcohol in short prisms melting at 74—75°. The corresponding *β-derivative* is deposited from alcohol in long, flat needles, and melts at 98—99°. Both compounds yield benzyl iodide when heated with hydriodic acid.

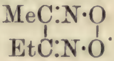
Metadibromobenzophenone is best prepared by heating benzophenone with the calculated quantity of bromine, together with a little iodine and water, in a sealed tube for four hours at 150°; after purification, the product crystallises from alcohol in broad, lustrous needles, and melts at 141°; the yield is 40 per cent. On gently heating with solution of hydroxylamine hydrochloride, an *oxime* is obtained, which is sparingly soluble in alcohol, and crystallises in slender needles; the yield is quantitative. The ketone is regenerated by the action of hydrochloric acid. No other oxime could be separated, and only the one compound is formed on treating the ketone with hydroxylamine and excess of alkali in the cold. All attempts to transform the oxime into a second modification were fruitless. From these results, it would appear that the power of forming two oximes is dependent on the symmetry, or otherwise, of the molecule. J. B. T.

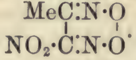
Action of Nitrogen Tetroxide on Aromatic Ketoximes and on Glyoximes. By R. Scholl (*Ber.*, **23**, 3490—3505).—The author has previously shown (Abstr., 1888, 443) that aliphatic ketoximes, when treated with nitrogen tetroxide in ethereal solution, are converted into pseudonitroles. The aromatic ketoximes behave in a somewhat similar manner, but the compounds obtained appear to correspond not with the fatty pseudonitroles, but with the dinitro-compounds obtained by the oxidation of the latter.

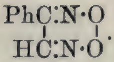
When benzophenonoxime (6 grams) is dissolved in ether (120 grams), and nitrogen tetroxide (3·5 grams) added, a brown solution is formed, which, after remaining for 10 minutes, is shaken with soda solution to remove nitric and nitrous acids, dried with calcium chloride, and allowed to evaporate in a vacuum. The product of the reaction is thus obtained in large, colourless, seemingly monosymmetric plates, which may be purified by the addition of water to the hot alcoholic solution. It has the composition $C_{13}H_{10}N_2O_4$, melts at 78—78·5°, decomposes with evolution of brown fumes at 98°, and is soluble in the common organic solvents. The simplest supposition is that it is *diphenyldinitromethane*, $CHPh_2(NO_2)_2$. That the nitro-groups have not entered the benzene ring is shown by the fact that on reduction it yields benzophenonoxime and benzylhydrylamine, $CHPh_2{\cdot}NH_2$; the formation of the first-named compound is not, however, altogether in favour of the supposition that the above substance is a dinitro-compound, and it is not impossible that both this compound and also the corresponding fatty dinitro-compounds may have a constitution expressed by the general formula $X_2{:}C{:}N{<}\genfrac{}{}{0pt}{}{O}{O{\cdot}NO_2}$, which agrees with the formula recently suggested by V. Meyer (Abstr., 1888, 702) for the pseudonitroles, namely, $X_2{:}C{:}N{\cdot}O{\cdot}NO_2$. For the sake of simplicity, however, these substances may, for the present, be regarded as dinitro-compounds.

Acetophenonoxime is acted on by nitrogen tetroxide in the same manner, but the oil obtained contains acetophenone, which could not be separated. On heating to 60°, the oil decomposes, with evolution of nitrous fumes.

Nitrogen tetroxide acts on aldoximes in quite a different manner; a simple oxidation taking place with formation of peroxides, thus, benzaldoxime yields *diphenylglyoxime peroxide*,  $\begin{array}{l}\mathrm{Ph\cdot C{:}N\cdot O}\\ \mathrm{Ph\cdot C{:}N\cdot O}\end{array}$, already described by Beckmann (Abstr., 1889, 980), under the name azodibenzenyl peroxide. The reaction is also similar to the formation of diphenyldinitrosacyl (dibenzoylglyoxime peroxide) by the oxidation of nitrosoacetophenone with nitric acid (Hollemann, Abstr., 1889, 49). As it appeared not impossible, from the author's experiments, that fulminic acid has the constitution  $\begin{array}{l}\mathrm{HC{:}N\cdot O}\\ \mathrm{HC{:}N\cdot O}\end{array}$ (see this vol., p. 282), the oxidation of the glyoximes has been more closely investigated.

Methylethylglyoxime is readily oxidised, both by alkaline potassium ferricyanide and by nitrogen tetroxide, the latter giving the best yield; the product of oxidation is a colourless, refractive, pleasant-smelling liquid, which boils at 115—116° (uncorr.) under 16·5 mm. pressure, and is miscible with the ordinary organic solvents, but is only sparingly soluble in water, and insoluble in alkalis. Its analysis agrees with the formula $C_5H_8N_2O_2$, and on distillation at the ordinary pressures it is partly decomposed into isocyanates, and is therefore, in all probability, *methylethylglyoxime peroxide*,  $\begin{array}{l}\mathrm{MeC{:}N\cdot O}\\ \mathrm{EtC{:}N\cdot O}\end{array}$. The corresponding *dimethylglyoxime peroxide* is readily obtained by oxidising dimethylglyoxime with nitrogen tetroxide in ethereal solution. It closely resembles the foregoing, but boils practically without decomposition at 222—223° under 726 mm. pressure.

The oxidation of monomethylglyoxime does not proceed as smoothly as in the two previous cases, an oil being obtained which is soluble in water, but very readily decomposes. It yields a yellow compound with soda, which also quickly becomes resinous. When the action of nitrogen tetroxide is allowed to continue for some time, a crystalline compound, of the formula $C_3H_3N_3O_5$, is also obtained, which has probably the constitution  $\begin{array}{l}\mathrm{MeC{:}N\cdot O}\\ \mathrm{NO_2\cdot C{:}N\cdot O}\end{array}$.

More stable products are obtained from monophenylglyoxime. This is best prepared by the action of a boiling solution of hydroxylamine hydrochloride on the crude sodium salt of isonitrosoacetophenone obtained by Claisen and Manasse's method (Abstr., 1887, 944). The oxidation cannot be carried out in alkaline solution, as the peroxide is at once decomposed by alkalis, but nitrogen tetroxide in ethereal solution readily effects the change. The resulting solution, after washing with water, is evaporated, the residue extracted with chloroform, and purified by precipitating its chloroform solution with light petroleum, or its acetic acid solution with water. Analysis and determination of the molecular weight by Raoult's method showed its formula to be $C_8H_6N_2O_2$, which agrees with the expected constitutional formula,  $\begin{array}{l}PhC{:}N{\cdot}O\\ \;\,| \qquad\;\; |\\ HC{:}N{\cdot}O\end{array}$. It has a bitter taste, melts with decomposition at 89—95°, is readily soluble in ether, acetone, chloroform, and acetic acid, more sparingly in alcohol, and insoluble in light petroleum. On recrystallising from alcohol, it is partially converted into benzaldehyde, and the odour of the latter and of phenylcarbamine is also observed on boiling it with water. With concentrated hydrochloric acid, it yields hydroxylamine. All attempts to displace the hydrogen atom by metals have been without success.

H. G. C.

Ethers of Benziloximes. By M. DITTRICH (*Ber.*, **23**, 3589—3608).—Attempts to prepare the methyl ether of γ-benziledioxime according to the method of Japp and Klingemann resulted in the formation of products identical with those from β-benziledioxime, showing that the γ-oxime had become converted into the more stable β-modification by the action of the alkali. The hydrochloride of β-benzildioxime methyl ether softens at 130°, and melts at 140—143°, instead of 130° as previously given.

α-Benziloxime methyl ether is prepared by the same method, and crystallises from alcohol in lustrous plates; it melts at 62—63°, is readily soluble in ordinary media, and does not combine with hydrochloric acid. No isomeric compound could be detected.

γ-Benziloxime methyl ether is obtained as an oily liquid, which boils at 219—220° under a pressure of 40 mm.; the distillate solidifies on cooling and may be crystallised from alcohol, from which it is deposited in prisms melting at 64—65°; by distillation under ordinary pressure, it is decomposed, and it does not combine with hydrochloric acid. No isomeric ether could be isolated. The α-ether is unaltered by boiling with hydrochloric acid, but on heating with this reagent in a sealed tube for several hours at 100°, it is converted into the γ-modification; by treating the latter compound in the same manner at 120—130°, it decomposes into benzile and ammonium chloride. Determinations by Raoult's method, with benzene as solvent, show that the methyl ethers of benziledioxime have identical molecular weights.

By the action of α-methylhydroxylamine on benzile at ordinary temperatures, a compound is obtained which crystallises from dilute alcohol, melts at 64°, and closely resembles γ-benzilemonoxime methyl ether in appearance and behaviour.

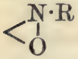
β-Methylhydroxylamine, $NHMe{\cdot}OH$, is prepared by heating β-benziledioxime methyl ether with hydrochloric acid; the *hydrochloride* is deposited in long, prismatic crystals which melt at 85—90°, and readily reduce alkaline copper solution. Neither the free base nor the hydrochloride reacts with benzile at ordinary temperatures, whilst on warming and in presence of excess of alkali, the base is completely decomposed. On heating the dibenzyl ethers of α- and β-benziledioxime with hydriodic acid, benzyl iodide is eliminated, proving that the compound contains the group $=NOH$. By the action of α-benzylhydroxylamine on γ-benzilemonoxime benzyl ether at 130—150°, a dibenzyl ether of α-benziledioxime, melting at 153—154°, is formed.

The same compound is also prepared from α-benzylhydroxylamine and α-benzilmonoxime, proving that the α-dibenzyl ether contains two $\vdots NOC_7H_7$ groups, and it is assumed that the methyl ethers have an analogous constitution.

Similar experiments with β-benzylhydroxylamine gave negative results.

Methyl iodide does not react with the non-basic methyl ether of α-benziledioxime, whilst by heating the second modification (α_2) with methyl iodide at 100°, it yields α-benziloxime methyl ether. On treating this same dimethyl ether (α_2) with hydriodic acid at 200°, methyl iodide and ammonia are formed.

These results show that the two α-benziledioxime methyl ethers are not geometrical isomerides, but are structurally different; it is suggested that whilst the non-basic modification (α_1) has the formula $RO\cdot N\colon CPh\cdot CPh\colon NOR$, the second ($\alpha_2$) contains the groups $\vdots NOR$ and



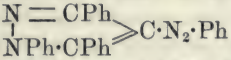
$<\overset{N\cdot R}{\underset{O}{|}}$; the above experiment with hydriodic acid tells, however, somewhat against this view. Benzile is formed by the action of amyl nitrite at ordinary temperatures on α- or γ-benzileoxime; α-benziledioxime is converted, to a considerable extent, into the β-dioxime; the latter by similar treatment yields crystals of an oxidation product which melt at 114° and give phenyl cyanate on distillation.
J. B. T.

Diphenyltriketone. By R. DE NEUFVILLE and H. V. PECHMANN (*Ber.*, **23**, 3375—3387).—Dibenzoylmethane is dissolved in chloroform and treated with bromine in molecular proportion, mixed with 3 parts of chloroform; during the addition of the bromine, a stream of dry air is drawn through the liquid in order to remove hydrogen bromide; the residue obtained, after evaporation of the chloroform, consists of *dibenzoylbromomethane*, $CHBrBz_2$; it crystallises from chloroform, on the addition of light petroleum, in lustrous needles, melts at 93°, and gives no coloration with ferric chloride. *Dibenzoylcarbinyl acetate*, $CHBz_2\cdot OAc$, is prepared by the action of anhydrous potassium acetate on the bromide; it crystallises from dilute alcohol in needles, melts at 94°, is insoluble in water or light petroleum, and gives a brown coloration with ferric chloride; the yield is 80 per cent. *Dibenzoylbromocarbinyl acetate*, $CBz_2Br\cdot OAc$, is obtained by the action of bromine on the previous compound; it is readily soluble in the ordinary media, and is deposited from chloroform, on the addition of light petroleum, in white crystals which melt at 101—102°; by heating the compound, either alone or in solution, acetic bromide is eliminated, and the triketone is formed.

Dibenzoyldibromomethane, CBr_2Bz_2, is prepared by the action of dibenzoylmethane on twice the molecular proportion of bromine; it crystallises from alcohol, and melts at 95°. The compound is completely decomposed by the action of alkalis, whilst small quantities of triketone are formed on boiling an alcoholic solution with silver oxide, carbonate, or nitrate; an acetic acid solution of potassium acetate causes a similar reaction. *Nitrosodibenzoylmethane*, $CBz_2\colon N\cdot OH$, is formed by treating dibenzoylmethane with amyl nitrite; it crystallises from a mixture of chloroform and light petroleum, melts at 146°, and is soluble in alkalis with a yellow colour.

Diphenyltriketone or *dibenzoyl ketone*, $CO(CO\cdot C_6H_5)_2$, is prepared by heating dibenzoylcarbinyl acetate, or by the action of nitrous acid on nitrosodibenzoylmethane; it crystallises from anhydrous light petroleum in golden-yellow needles, melts at 69—70°, and boils at 247—248° under a pressure of 60 mm., and at 289° under a pressure of 175 mm.; is very hygroscopic, and readily dissolves in all solvents except water.

"*Diphenyltriketone hydrate*," *dibenzomethylene glycol*, $CBz_2(OH)_2$, is formed as a white, flocculent precipitate on dissolving the ketone in alcohol or glacial acetic acid and adding water; it melts at 90°, and is also formed by boiling dibenzoylbromocarbinyl acetate with glacial acetic acid, or by the action of potassium acetate on dibenzoyldibromomethane. Chemically, the hydrate resembles the ketone; both give a brilliant blue coloration on the addition of sulphuric acid to a benzene solution. The hydrate readily dissolves in alkalis with the formation of phenylbenzoylhydroxyacetic acid, $OH\cdot CPhBz\cdot COOH$, which has not yet been isolated. After the solution has remained for some time, this compound is decomposed by the further action of the alkali; part yields benzoic acid and phenylhydroxyacetic acid, whilst carbonic anhydride and benzoïn are produced from the remainder.

On treating the triketone with phenylhydrazine in molecular proportion at ordinary temperatures, a compound is deposited which crystallises from a mixture of chloroform and light petroleum in aggregates of almost colourless needles, melts at 135°, and acquires a red colour after remaining in contact with the air. The substance has the formula $C_{21}H_{16}N_2O_2$, but it is uncertain whether it is really a phenylhydrazone; it dissolves in concentrated sulphuric acid with a yellow colour, but the solution is not affected by ferric chloride or potassium dichromate (Bülow's reaction). By the action of excess of phenylhydrazine on the triketone, or on the previous compound, two substances are obtained and may be separated by treatment with benzene at ordinary temperatures; the one crystallises in yellow needles, melts at 223°, and has not yet been further investigated. The second compound is soluble in benzene, and consists of *benzenazotriphenylpyrazole*,  $\left.\begin{array}{l}N{=}CPh\\ NPh\cdot CPh\end{array}\right>C\cdot N_2\cdot Ph$; it crystallises from alcohol in orange-red prisms, and melts at 156—157°.

Diphenyltriketonanilide, $NPh{:}CPh\cdot CBz(OH)_2$, is formed by treating the triketone with two parts of aniline at the ordinary temperature; it crystallises from benzene, on the addition of light petroleum, in yellow, concentric needles, melts at 99—100°, and gives a blue coloration with sulphuric acid and benzene. On boiling the triketone with alcoholic solution of aniline, the *dianilide*, $C(OH)_2(CPh{:}NPh)_2$, is obtained, crystallising from benzene in yellow pyramids which melt at 148°.

Diphenyltrinitrosopropane, $OH\cdot N{:}C(CPh{:}N\cdot OH)_2$, is obtained as a white, crystalline powder from nitrosodibenzylmethane and hydroxylamine; it is insoluble in water, but readily dissolves in alkalis and organic menstrua, and melts at 185—186°. A second compound is formed in small quantity; this crystallises in plates, melts at 141°, is insoluble in alkalis, and has not yet been further investigated.

Attempts to prepare other triketones from acetophenone, benzoylacetone, acetylacetone, and ethyl acetoacetate have been unsuccessful.

J. B. T.

Cresolcinnamic and Metacresolglycollic Acids. By A. OGLIALORO and O. FORTE (*Gazzetta*, **20**, 505—513).—The cresolcinnamic acids were prepared by heating the corresponding sodium cresolglycollates with benzaldehyde and acetic anhydride.

Orthocresolcinnamic acid is obtained pure by decomposing its barium salt. It crystallises from a dilute alcoholic solution in small, white prisms, melts at 167—168°, and is very soluble in warm alcohol, moderately in ether, chloroform, and benzene. The *barium* salt, $(C_{16}H_{13}O_3)_2Ba + H_2O$, dissolves very sparingly in hot water, and may be obtained crystallised by evaporating the solution. The *silver* salt, $C_{16}H_{13}O_3Ag$, decomposes at 100°. The *methyl* salt, $C_{16}H_{13}O_3Me$, crystallises from dilute alcohol in colourless plates, melts at 61°, and dissolves very freely in alcohol and ether, and moderately in light petroleum and chloroform, but is insoluble in water; a brominated derivative, $C_{17}H_{12}Br_6O_3$, may be obtained by adding bromine to saturation to the methyl alcoholic solution of this compound, and heating the mixture for a few hours. It crystallises in brilliant, yellow scales, and melts at 231°.

Metacresolglycollic acid, $C_9H_{10}O_3$, is prepared by melting a mixture of metacresol and chloracetic acid in molecular proportion, and adding a quantity of aqueous soda (sp. gr. = 1·3) quadruple that of the cresol taken. It crystallises from boiling water in minute, white needles, and melts at 102°. The *barium* salt, $(C_9H_9O_3)_2Ba + 6H_2O$, crystallises from an aqueous solution in nodules consisting of very fine, white needles.

Metacresolcinnamic acid crystallises in white needles, melts at 155°, and dissolves freely in alcohol and ether. The *silver* salt is white and anhydrous, and is not altered by exposure to light. The *barium* and the *methyl* salts are uncrystallisable compounds; the latter is a viscid substance yielding a brominated derivative, $C_{17}H_{16}Br_2O_3$, which crystallises in colourless, rhombic tables, and melts at 109°.

Paracresolcinnamic acid crystallises in white needles, melts at 159—160°, and dissolves in alcohol, ether, and benzene. The acid cannot be completely purified, but a *silver* salt of the theoretical composition may be isolated. The *barium*, *magnesium*, and *methyl* salts are uncrystallisable; the last is a viscid product, and yields a brominated derivative, $C_{17}H_{16}Br_2O_3$, which crystallises from methyl alcohol in brilliant, colourless, rhombic tables melting at 124—125°.

S. B. A. A.

Sulphides of β-Naphthol. By S. ONUFROWICZ (*Ber.*, **23**, 3355—3373).—β-Naphthol sulphide or β-hydroxynaphthyl sulphide, $S(C_{10}H_6{\cdot}OH)_2$, is prepared by the action of either sulphur dichloride or of sulphur and lead oxide on β-naphthol.

The *α-sodium* derivative, $S(C_{10}H_6{\cdot}ONa)_2 + 6H_2O$, is obtained by dissolving the sulphide in soda; it crystallises in colourless, concentric needles, is readily soluble in water or alcohol, and has an alkaline reaction. The corresponding *calcium* and *barium* salts are colourless and crystalline, and, like the salts of the heavy metals, are very sparingly soluble in water. The *diethyl* derivative,

$$S(C_{10}H_6{\cdot}OEt)_2,$$

is prepared by the action of the calculated quantity of ethyl iodide and potash on the sulphide; it crystallises from benzene in long, slender, wax-like, lustrous needles, melts at 189°, and is not acted on by silver nitrate or mercuric oxide.

β-Naphthylamine and β-naphthol are formed by the action of ammonia on β-naphthol sulphide, whilst β-naphthol is the sole product when the sulphide is treated with cuprous chloride or silver chloride. By the action of silver nitrate or of mercuric oxide on the sulphide, a compound is obtained which crystallises from dilute alcohol in stellate groups of ruby-red plates, and melts at 164°; the yield is 25—30 per cent. of the sulphide employed. This substance has the formula $C_{20}H_{12}SO_2$, and is not acted on when boiled with either soda or glacial acetic acid; when heated to 200°, it yields hydrogen sulphide and β-naphthol, whilst, by reduction with zinc-dust and glacial acetic acid, β-naphthol sulphide is regenerated. By the action of potassium dichromate and sulphuric acid, part of the sulphide is completely oxidised, and part remains unchanged; with dilute nitric acid, sp. gr. 1·18, phthalic acid is the sole product.

β-Naphthol sulphide is decomposed by concentrated nitric acid; but on dissolving the diethyl derivative in 10 parts of glacial acetic acid, adding 5 parts of fuming nitric acid, and cooling well with ice, *dinitronaphthyl ethyl ether*, $C_{10}H_5(NO_2)_2{\cdot}OEt$ [$OEt : (NO_2)_2 = 2 : 1' : 4'$], is obtained, and may be purified by treatment with benzene; it crystallises from dilute alcohol in long, slender, pale-yellow, silky needles, melts at 215°, and is not acted on by aqueous soda. The yield is 30 per cent. When heated with dilute nitric acid at 160—170°, dinitronaphthalenedicarboxylic acid [$(COOH)_2 : (NO_2)_2 = 1 : 2 : 3 : 6$] is produced.

Dinitramidonaphthalene [$NH_2 : (NO_2)_2 = 2 : 1' : 4'$] is formed by heating the above ethyl derivative with concentrated alcoholic ammonia at 220—225°; it is very sparingly soluble, and crystallises from toluene in slender, yellow needles which blacken at about 250°, but do not melt. When β-ethoxynaphthyl sulphide is treated with concentrated nitric acid at very low temperatures, the product, after washing with ice water, dissolved in benzene and the solution cooled, *ethoxydinitronaphthyl sulphide*, $S[C_{10}H_5(NO_2){\cdot}OEt]_2$, is deposited in slender, golden-yellow needles which melt at 235°. After some time, a further deposit is obtained from the mother liquor; this is dissolved in ether, and crystallises, on the addition of light petroleum, in slender, pale-yellow needles; it melts at 202°, and is readily soluble in alcohol or benzene, both at ordinary temperatures and on warming. This substance has the formula $C_{24}H_{20}N_2S_2O_6$, and is probably a dinitro-derivative.

β-Naphthol bisulphide or *β-hydroxynaphthyl bisulphide* is obtained by heating β-naphthol with sulphur at 175—180° for 24 hours; after purification, it crystallises from benzene in slender, yellow needles, melts at 169°, and is very sparingly soluble in ordinary menstrua. When heated to 360°, it decomposes into hydrogen sulphide and β-naphthol; it is soluble in dilute, and gives a red colour with concentrated alkalis. The yield is 10 per cent. The same compound, together with a considerable quantity of the monosulphide, is also formed by the action of sulphur chloride at 0° on β-naphthol dissolved in benzene; the yield is about the same as before. The best results are obtained by heating a solution of the sulphide with half the molecular proportion of sulphur bromide for an hour on the water-bath; in this manner 10 grams of β-naphthol yielded 5 grams of pure bisulphide. *β-Ethoxynaphthyl bisulphide*, $S_2(C_{10}H_6{\cdot}OEt)_2$, is prepared in a similar manner to the corresponding monosulphide derivative; it crystallises from alcohol in greyish needles, and melts at 158·5°. The *diacetate*, $S_2(C_{10}H_6{\cdot}OAc)_2$, forms a yellow, hard, crystalline mass which melts at about 140°, and is soluble in ether, alcohol, benzene, and glacial acetic acid. The *dibenzoate*, $S_2(C_{10}H_6{\cdot}OBz)_2$, crystallises from benzene in greenish plates or prisms, and melts at 187°.

On heating the bisulphide with recently reduced copper at 230—240°, it yields β-dinaphthol, m. p. 212°; the bisulphide is not altered by boiling with copper and xylene or cumene.

α-Naphthol trisulphide, $S_3(C_{10}H_6{\cdot}OH)_2$, is obtained by the action of sulphur chloride on α-naphthol, and is a pale yellow, amorphous substance which blackens at 220°, and is very readily soluble in dilute aqueous soda, but almost insoluble in organic media. The corresponding *benzoate*, $S_3(C_{10}H_6{\cdot}OBz)_2$, is a greyish powder melting at 194°.

When benzene is mixed with 0·5 part of sulphur chloride and 0·05 part of iodine, heated in a sealed tube for 100 hours at 115—125°, and the product boiled with benzene, toluene, carbon bisulphide, and xylene successively, a yellow, hard, amorphous mass remains which is slightly soluble in xylene, and has the formula S_6Ph_2.
J. B. T.

Ethereal Oil of Asafœtida. By F. W. SEMMLER (*Ber.*, **23**, 3530—3533).—Up to the present, it has not been found possible to separate crude asafœtida into its constituents by fractional distillation, but the author finds that this may be readily carried out under diminished pressure. Thus, under 9 mm., two specimens of crude oil of sp. gr. 0·9843 at 22° and 0·9789 at 12° respectively, gave, on repeated fractionation, four chief fractions distilling below 65°, at 80—85°, 120—130°, 133—145°.

The fraction distilling below 65°, obtained from both specimens, had the same qualitative composition, but the constituents were present in different quantities, thus causing a difference in the specific gravity. On treatment with potassium in a vacuum until no more gas is evolved, and then distilling, a colourless, pleasant-smelling oil is obtained, which has the composition $C_{10}H_{16}$; it is a mixture of two different terpenes, one of which yields a liquid, and the other a solid dibromide. It is contained ready formed in the oil, and may also be obtained from the fraction distilling below 65° by adding mercuric chloride until no further precipitate is formed, and distilling in a current of steam. The first sample of oil was thus found to contain 6 per cent., and the second 8 per cent., of the mixture of terpenes.

The fraction 133—145° was treated with sodium in a vacuum, and on distillation under 9 mm. pressure, a colourless oil passed over at 123°, which had a pleasant, lavender-like odour, a sp. gr. of 0·9241 at 15°, and the composition $C_{15}H_{24}$. It belongs, therefore, to the group of sesquiterpenes, and forms a *hydrochloride*, $C_{15}H_{24},2HCl$.

These two fractions consist chiefly of substances free from sulphur, the compounds containing the latter being found in the second and third fractions, which are, at present, being more closely investigated.

H. G. C.

Indian Geranium Oil: Geranaldehyde and Geranic Acid. By F. W. SEMMLER (*Ber.*, **23**, 3556—3557; see also Abstr., 1890, 951).—In the previous paper, it was shown that geraniol, on treatment with chromic acid and distillation in a current of steam, yields an aldehyde, $C_{10}H_{16}O$, which may be termed *geranaldehyde*. If the residue, after removal of the aldehyde, is treated with phosphoric acid and again distilled in a current of steam, a small quantity of an oil is obtained which has an acid reaction. It may be prepared much more readily by making an emulsion of 6 grams of geranaldehyde in 500 grams of water, gradually adding a solution of 13·5 grams of silver oxide in dilute ammonia, acidifying with a slight excess of phosphoric acid, and distilling in a current of steam. The distillate is neutralised with soda, evaporated to dryness, the residue extracted with boiling absolute alcohol, and the latter expelled from the filtrate. The residue is taken up with water and precipitated by means of silver nitrate as the *silver* salt; this has the composition $C_{10}H_{15}O_2Ag$. *Geranic acid* is a thin oil.

The alcohol and aldehyde also occur in other oils, of which a more detailed account will be given later. (Compare also following abstract.)

H. G. C.

German and Turkish Rose Oil. By T. POLECK and C. ECKART (*Ber.*, **23**, 3554—3555; see also Markovnikoff, this vol., p. 219).—The first product which passes over in the distillation of German rose oil is ethyl alcohol, about 5 per cent. of which is present. Terpenes could not be identified. After removing stearoptene, the German rose oil was distilled under diminished pressure, when it passed over almost entirely at 110—120° (14 mm.). Its boiling point at atmospheric pressure was found to be 215°. The Turkish oil behaves in a similar manner, both eleoptenes being lævorotatory, the German variety having a sp. gr. of 0·8837 at 11°, and the Turkish, 0·8813 at 12°.

The analyses of the liquid portions of both oils indicated the formula $C_{10}H_{18}O$. This compound has the characteristics of a primary alcohol with two ethylene linkages, both with regard to the molecular refraction and its behaviour towards bromine. Its sodium derivative, chloride, iodide, and benzoate have been analysed. On oxidation, it yields, first, an aldehyde, $C_{10}H_{16}O$, and then an acid, $C_{10}H_{16}O_2$. Phosphoric anhydride and zinc chloride abstract the elements of water, forming a mixture of two different terpenes, $C_{10}H_{16}$, which differ considerably in their boiling point. If the action takes place below 0°, the higher boiling terpene is strongly dichroic. The only products of further oxidation found were carbonic anhydride, formic, acetic, and oxalic acids.

The properties of the liquid constituent of both the German and Turkish oils correspond exactly with those of geraniol, the chief constituent of Indian geranium oil (Semmler, Abstr., 1890, 951, and preceding abstract), and a direct comparison of the aldehydes has shown their actual identity. The eleoptene of rose oil, therefore, also contains an open chain of carbon atoms, which, on elimination of water, unite to form a closed chain. H. G. C.

Phenolic Acid from Camphor. By P. CAZENEUVE (*Compt. rend.*, **111**, 743—745).—Monochlorcamphor is treated with six times its weight of concentrated sulphuric acid at 50° for 30 hours and the product is poured into cold water. After some time, the liquid is filtered, heated, saturated with barium carbonate, and concentrated. Amethylcamphophenolsulphone (Abstr., 1890, 1153) and the barium salt of the new acid crystallise together. They can be separated by crystallisation from alcohol of 70°, in which the barium salt remains dissolved, and it can afterwards be purified by crystallisation from water.

The barium salt crystallises in nacreous plates, and when treated with sulphuric acid it yields amethylcamphophenolsulphonic acid, $OH\cdot C_9H_{12}O\cdot SO_3H$, isomeric with the sulphone, a colourless, syrupy, uncrystallisable liquid, with a bitter, astringent, acid taste, and an odour recalling that of solutions of oak-bark. It is very soluble in water, alcohol, and ether, has no action on polarised light, and distils partially without decomposition under reduced pressure. Solutions of the barium salt gave a magnificent, blue coloration with ferric chloride. If the salt is boiled with acetic anhydride for 15 minutes, it yields an acetyl derivative, $OAc\cdot C_9H_{12}O\cdot SO_3H$, the barium salt of which has no action on ferric chloride. When treated with potassium hydroxide, the original phenolic acid is formed. C. H. B.

Action of Camphoric Anhydride on Benzene. By E. BURCKER (*Bull. Soc. Chim.* [3], **4**, 112—113).—Under conditions similar to those by which benzoylpropionic acid is formed, camphoric anhydride and benzene react in presence of aluminium chloride to form a compound, $C_{16}H_{20}O_3$, which is separated from its sodium salt by treatment with hydrochloric acid as very light scales; it is soluble in alcohol, chloroform, ether, and acetic acid, but only sparingly in benzene, and almost insoluble in water. It melts at 125—126°, but if this temperature is passed it no longer solidifies on cooling, but remains as a syrup, and decomposes at a higher temperature without boiling. The compound behaves as a monobasic acid. Solutions of the alkaline hydroxides dissolve it, and the salts formed by it with cobalt, nickel, copper, and silver crystallise easily. With phenylhydrazine, it yields a yellow, crystalline derivative. Further work is being carried on to determine its constitution.

T. G. N.

Crystalline Principle from the Bark of Diospyros virginiana. By W. SCHLEIF (*J. Pharm.* [5], **22**, 469—471; from *Amer. J. Pharm.*, 1890, 390).—The powdered root is extracted with light petroleum, by which a yellow solution is obtained, yielding a waxy residue on evaporation. The powder is then treated with ether and the solution distilled, when a deep-red, crystalline residue is left; this is dissolved in hot alcohol and treated with an alcoholic solution of lead acetate, which removes the colouring matter only. After filtration, the liquid is treated with hydrogen sulphide, again filtered, and the still reddish, alcoholic solution is digested with animal charcoal on the water-bath, and concentrated by distilling off the alcohol; the crystals which separate are purified by repeated recrystallisation from alcohol until the dry product has a yellowish-grey colour. The crystalline mass thus obtained sometimes contains crystals 0·2 mm. long; these are soft, and waxy in appearance when moist. The dry substance is light brown in colour and granular in texture, with a peculiar odour, and a slightly astringent taste. It is soluble in alcohol, ether, and chloroform, very little soluble in water, and not at all in light petroleum. At 258° it takes a deeper tint, and at 262° it melts with apparent decomposition. The compound has a neutral reaction; it does not dissolve on boiling with dilute hydrochloric acid or in dilute potash solution; it burns on platinum foil without leaving any residue. Its alcoholic solution is not precipitated by alcoholic solution of lead acetate or of ammonia. It dissolves in glacial acetic acid. Its composition corresponds with the formula $C_{39}H_{67}O_{10}$. J. T.

β-Picoline. By A. LADENBURG (*Ber.*, **23**, 3555—3556).—In reply to Stoehr's criticisms of the author's previous paper on this subject (Abstr., 1890, 1432), Ladenburg states that the facts from which his conclusions were drawn were obtained in personal communications from Stoehr, and that, as there stated, the truth of those statements is now being experimentally investigated. H. G. C.

Derivatives of Toluquinoline and Metaxyloquinoline. By E. NOELTING and E. TRAUTMANN (*Ber.*, **23**, 3654—3683).—Quinoline is dissolved in 10 parts of sulphuric acid (100 per cent.) and treated with the theoretical quantity of fuming nitric acid also dissolved in sulphuric acid; enough fuming sulphuric acid, containing 20—25 per cent. of sulphuric anhydride, is added to combine with the water contained in the nitric acid and also with that formed during the reaction; the mixture is either gently heated, or allowed to remain for several days at ordinary temperatures; in this manner only the two mononitro-derivatives are formed.

Nitroparatoluquinoline, $C_9NH_5Me{\cdot}NO_2$ [$Me : NO_2 = 3 : 4$], is prepared by the action of nitric acid on paratoluquinoline in presence of sulphuric acid; it crystallises from alcohol in pale-yellow needles, melts at 116—117°, and is readily soluble in organic menstrua. The salts are crystalline, but readily undergo dissociation in presence of water. The proof of the above formula consists in the fact that the corresponding amido-derivative does not yield methylphenanthroline by the action of glycerol and picric acid. The *methiodide* crystallises from alcohol in long, yellow needles; on allowing these to remain in contact with the mother liquor, rhombohedra are formed; from water the compound is deposited in colourless rhombohedra, which become yellow at 100°; both forms melt at 189—190°.

Amidoparatoluquinoline is prepared by the reduction of the above nitro-derivative with iron and acetic acid; it crystallises from water or dilute alcohol in yellow needles, and melts at 145°; the yield is 90 per cent. of theory. The hydrogen salts are red, whilst the normal salts are almost colourless, but are red in aqueous solution. The *acetyl derivative* crystallises from water in white needles, melts at 160°, and yields colourless salts with acids.

Hydroxyparatoluquinoline, $C_9NH_5Me{\cdot}OH$, is prepared by the action of sodium nitrite on the amido-compound; it crystallises from alcohol in flat needles, melts at 230°, sublimes without decomposition, and is not volatile with steam. The same compound is also obtained by the action of fuming sulphuric acid at 90° on paratoluquinoline; the resulting sulphonic acid being then fused with potash. It forms well-characterised salts with acids and alkalis, and yields a *hydroxyazo-derivative* with diazobenzene chloride, which is deposited from alcohol in small, red needles melting at 176°.

Nitroso-hydroxyparatoluquinoline or *oxyparatoluquinoline oxime*, $C_9NH_4Me(NOH)O$, is obtained by the action of nitrous acid on the hydroxy-derivative at low temperatures; it crystallises from water in yellow needles and from alcohol in yellow plates, which decompose above 200° without melting. The *hydrochloride* is sparingly soluble in hydrochloric acid, and crystallises in yellow needles; the *sodium salt* is deposited in small, yellow plates. The nitroso-compound yields a stable green dye with iron mordanted cloth, this property is probably due to the presence of a salt-forming group in the peri-position [4 : 1′] to nitrogen; thus, whilst the three orthohydroxytoluquinolines (see below) and orthoquinone oximes give dyes with mordants, paraquinone oximes only do so if they contain the NOH group in the position 1.

Orthonitrohydroxyparatoluquinoline,

$$NO_2{\cdot}C_9NH_4Me{\cdot}OH\ [NO_2 : OH : Me = 1 : 3 : 4],$$

is prepared by the oxidation of the oxime with potassium ferricyanide, and crystallises from dilute acetic acid or alcohol in yellowish-brown plates, which decompose while melting.

Orthohydroxymetatoluquinoline, $C_9NH_5Me{\cdot}OH$ [OH : Me = 1 : 2], is prepared from amidorthocresol, [OH : NH_2 : Me = 1 : 2 : 6], glycerol, and picric acid; it crystallises from dilute alcohol in long needles, melts at 72—74°, is volatile with steam, and, in contact with copper oxide, colours the flame green; the yield is 80 per cent.

Nitroso-orthoxymetatoluquinoline, $C_9NH_4Me(NOH)O$ [O : Me : NOH = 1 : 2 : 4], is prepared by the action of sodium nitrite on the preceding compound, and it is deposited from alcohol or dilute acetic acid in yellow needles; it decomposes at about 200° without melting, and has no tinctorial properties. Soluble salts are formed with acids and bases. *Nitrorthohydroxymetatoluquinoline* is obtained from the preceding compound by oxidation with potassium ferricyanide in alkaline solution; it crystallises from alcohol in red needles and from benzene in yellow needles, melts at 192—193°, yields salts with acids and bases, and dyes mordanted cloth.

Orthohydroxymethylquinoline, $C_9NH_5Me{\cdot}OH$ [OH : Me = 1 : 4], is prepared from amidoparacresol, [OH : NH_2 : Me = 1 : 2 : 4]; it crystallises from dilute alcohol in long, colourless needles, melts at

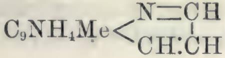
122—124°, and gives a yellow dye with aluminium mordants; the yield is 65 per cent. of theory. *Nitroso-orthoxymethylquinoline*, $C_9NH_4MeO:NOH$ [O : NOH : Me = 1 : 3 : 4], resembles the previously described isomerides, and dyes mordanted cloth; on oxidation, it yields the corresponding *nitro*-derivative, which crystallises from alcohol in slender, yellow needles melting at 205—206°; yellow colours are obtained with aluminium mordants.

Nitroparatoluquinoline, $C_9NH_5Me{\cdot}NO_2$ [Me : NO_2 = 3 : 4], is obtained from nitroparatoluidine, [NH_2 : NO_2 : Me = 1 : 3 : 4]; it crystallises from alcohol, and melts at 116—117°; the yield is 65 per cent. The corresponding *amido-*, *acetyl*, and *hydroxy*-derivatives have been prepared and closely resemble the previously described isomerides. *Orthonitroparatoluquinoline*, $C_9NH_5Me{\cdot}NO_2$ [NO_2 : Me = 1 : 3], is prepared from nitroparatoluidine [NH_2 : NO_2 : Me = 1 : 2 : 4], and crystallises from water in pale-yellow needles, melts at 122°, and does not combine with methyl iodide; the yield is 60 per cent. The salts crystallise readily, but dissociate with water. *Orthamidoparatoluquinoline* is prepared from the preceding compound by reduction with ammonium sulphide; it crystallises in slender needles, melts at 62—64°, sublimes without decomposition, and is volatile with steam. The *hydrochloride* forms orange needles. The *acetyl derivative* is obtained from water or dilute alcohol in large plates melting at 91—92°. It yields salts which readily crystallise. The hydroxy-derivative is prepared by means of the diazo-reaction, and is identical with the compound obtained from toluquinolinesulphonic acid [SO_3H : Me = 1 : 3] by fusion with potash. The *nitroso*-compound, $C_9NH_5Me(NOH)O$ [O : Me : NOH = 1 : 3 : 4], is very sparingly soluble, and crystallises in brown plates, which decompose at 200°, and do not dye. The nitro-derivative could not be obtained.

Orthamidochloroparatoluquinoline, $C_9NH_4MeCl{\cdot}NH_2$ [NH_2 : Me : Cl = 1 : 3 : 4], is formed, together with amidotoluquinoline, by the reduction of the nitro-compound with tin and hydrochloric acid; it crystallises from alcohol in silky, lustrous needles, melts at 129—130°, and does not combine with diazo-compounds. The *monacid salts* are orange-yellow and readily undergo dissociation. The *hydrochloride* is sparingly soluble. The *acetyl derivative* is deposited from dilute alcohol in lustrous needles melting at 136—137°.

Nitrorthotoluquinoline, $C_9NH_7Me{\cdot}NO_2$ [Me : NO_2 = 1 : 2], is prepared by the nitration of orthotoluquinoline, and crystallises in pale-yellow needles melting at 93°. It is volatile with steam, does not combine with methyl iodide, and on heating with alcoholic potash gives a violet colour, changing to red and finally to dirty brown on exposure to air. The yield is almost theoretical. The same compound is synthetically prepared from nitrotoluidine [NH_2 : Me : NO_2 = 1 : 2 : 5]. The salts readily undergo dissociation.

Amidorthotoluquinoline is obtained by reduction of the preceding compound with iron and acetic acid, and crystallises from water or dilute alcohol in long, yellow needles melting at 143°. The *hydrochloride* is red, the *dihydrochloride*, yellow.

Methylphenanthroline,  [Me : CH : N = 1 : 3 : 4],

$$C_9NH_4Me{<}\begin{matrix}N{=}CH\\ \vert\\ CH{:}CH\end{matrix}$$

is obtained by the action of glycerol and sulphuric acid on the amine, and is deposited from light petroleum in small crystals melting at 95—96°. It is identical with the compound obtained by synthesis from metatoluylenediamine. The *picrate* melts at 252—253°.

Acetamidorthotoluquinoline crystallises from water in silky, lustrous needles, and melts at 187°. Hydroxyorthotoluquinoline, from the amide, crystallises from dilute alcohol in colourless needles, and melts at 262—263° on rapidly heating. A compound identical with this has previously been prepared from orthotoluidinesulphonic acid [$SO_3H : NH_2 : Me = 1 : 3 : 4$]. With diazobenzene chloride, a *hydroxyazo*-derivative is formed, crystallising from alcohol in red needles melting at 138—139°, and soluble in aqueous alkalis. The *nitroso*-compound, $C_9NH_4Me(NOH)O$ [$Me : NOH : O = 1 : 3 : 4$], crystallises from alcohol in yellowish-brown plates, decomposes above 200° without melting, and gives "lakes" with the heavy metals. The *nitro*-derivative is formed on oxidation, and is deposited in orange needles which melt at 181—182°, and do not dye.

Azorthotoluquinoline, $N_2(C_9NH_5Me)_2$ [$Me : N = 1 : 4$], is formed, together with amidotoluquinoline, by the reduction of nitrorthotoluquinoline with iron and hydrochloric acid; it crystallises from glacial acetic acid in orange needles, and melts at 260°. The *hydrochloride* is readily obtained in red crystals. On reduction with stannous chloride or alcoholic ammonium sulphide, a compound is formed which is insoluble in water, yields red salts, and has not yet been further investigated.

Azoxyorthotoluquinoline, $ON_2(C_9NH_5Me)_2$, is formed, together with the azo-derivative, and may be separated by crystallisation from hydrochloric acid, in which it is tolerably soluble; it may be prepared directly by the incomplete reduction of nitrotoluquinoline, and crystallises from alcohol in slender, yellow needles melting at 201°. The *hydrochloride* is deposited in very slender, lemon-yellow needles; all the salts are readily dissociated. When heated with 10 parts of sulphuric acid at 110—115°, a compound is formed which is probably *hydroxyazotoluquinoline*, $C_9NH_5Me{\cdot}N_2{\cdot}C_9NH_5Me{\cdot}OH$ [$Me : OH : N = 1 : 3 : 4$]; it is insoluble in alkalis, as is also the corresponding compound [$Me : N = 1 : 4$; $Me : N : OH = 1 : 3 : 4$] from amidotoluquinoline and hydroxytoluquinoline.

Nitrometaxyloquinoline, $C_9NH_4Me_2{\cdot}NO_2$ [$Me : Me : NO_2 = 1 : 3 : 4$], is obtained by nitrating metaxyloquinoline; it crystallises from alcohol in long, yellow needles, melts at 107—108°, is scarcely volatile with steam, and does not combine with methyl iodide. The salts are decomposed by water. The constitution of the compound is shown by its synthesis from nitroxylidine [$NH_2 : Me : Me : NO_2 = 1 : 2 : 4 : 5$]; it gives no coloration with alcoholic potash. *Amidometaxyloquinoline* is formed by the reduction of the preceding compound with iron and acetic acid, or stannous chloride and hydrochloric acid; it crystallises from dilute alcohol in long, yellow needles, and melts at 91°. The *acetyl* derivative is deposited from water in colourless needles which melt at 201°. *Hydroxymetaxyloquinoline*, from the amido-compound and nitrous acid, crystallises from chloroform in white plates, and melts at 197—198°. On sublimation, it is obtained in small needles, and salts are formed with acids and bases. The *hydrochloride* crystallises in yellow needles. J. B. T.

2-Methylquinaldine. By E. Rist (*Ber.*, **23**, 3483—3487).—The author has already shown (Abstr., 1890, 1324) that the so-called metamethylquinaldine obtained by Döbner and v. Miller from paraldehyde and metatoluidine (Abstr., 1884, 183), and which might, therefore, have either the meta- or ana-constitution, is converted by oxidation into the quinaldinecarboxylic acid prepared by Döbner and v. Miller from metamidobenzoic acid and aldehyde. The *hydrochloride* of the latter acid forms small, characteristic tablets sparingly soluble in cold, readily in hot water, whilst the *platinochloride*, $4(C_{11}H_9NO_2,HCl),PtCl_4$, crystallises in reddish-yellow, monosymmetric prisms readily soluble in water. Its *silver* salt, $C_{11}H_8NO_2Ag$, crystallises from hot water in microscopic crystals soluble in ammonia and nitric acid.

To ascertain whether these compounds are really 2-derivatives, the author subjected Gerdeissen's 2-amidoquinaldine (Abstr., 1889, 520) to Sandmeyer's reaction. The ordinary procedure cannot be adopted in this case, as the compound appears to form a stable nitrite. The mixture must be diazotised below 0°, allowed to remain, and then added to the freshly prepared cuprous cyanide on the water-bath in small quantities and with vigorous shaking. As soon as gas ceases to come off, the hot liquid is filtered, saturated with soda, and the precipitate recrystallised from water. The *nitrile* thus obtained forms silky needles melting at 82°, and crystallises with approximately 2 mols. H_2O, which are given off on drying over sulphuric acid, the melting point then becoming 104°. It is volatile in a current of steam, soluble in the ordinary solvents and in acids, and may be distinguished from the otherwise similar 2-amidoquinoline by the fact that it yields a colourless or pale-yellow solution with alkalis. On hydrolysis, it is converted into a quinaldinecarboxylic acid, which is identical with the acid already described. It follows, therefore, that both this acid and the methylquinaldine from which it was prepared have, in reality, the meta- and not the ana-constitution.

H. G. C.

Constitution of β-Quinaldinesulphonic Acid. By B. Richard (*Ber.*, **23**, 3488—3490).—By the action of sulphuric acid on quinaldine, Döbner and v. Miller obtained a mixture of three sulphonic acids, two of which were shown to be ortho- and para-quinaldinesulphonic acids, whilst the constitution of the third, known as the β-acid, was not ascertained (Abstr., 1884, 183). In order to determine its constitution, the author converted it by the usual reactions into the corresponding nitrile and carboxylic acid, both of which were found to be identical with the 2-cyanoquinaldine and quinaldine-2-carboxylic acid described by Rist (see preceding abstract). The acid from which they are prepared must, therefore, be quinaldine-2-sulphonic acid. H. G. C.

Condensation of Metanitrobenzaldehyde with Quinaldine. By W. Wartanian (*Ber.*, **23**, 3644—3653).—Metanitrobenzaldehyde is heated for 3—4 hours on the water-bath with rather more than 1 part of quinaldine, zinc chloride being added from time to time in small portions; after purification and crystallisation from alcohol, a product is obtained which melts at 124—126°, and consists of a mixture of *metanitrobenzylidenequinaldine*,

$$C_9NH_6{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2\ [CH = 2';\ CH : NO_2 = 1 : 3],$$

and of the aldol compound, $C_9NH_6{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NO_2$; the former substance may be separated by treatment with acetic anhydride at 135°; it is deposited from a mixture of benzene and light petroleum in yellow, nodular, crystalline aggregates, and melts at 139°. The *hydrochloride* forms long, rectangular crystals; the *nitrate* crystallises in pale-yellow, lustrous needles; the *picrate* is deposited in lemon-yellow, interlaced needles: the *platinochloride*, $(C_{17}H_{12}N_2O_2)_2,H_2PtCl_6 + 1\frac{1}{2}H_2O$, is crystalline. When reduced with stannous chloride and hydrochloric acid, *metamidobenzylidenequinaldine*, $C_9NH_6{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NH_2$, is produced, crystallising from a mixture of benzene and light petroleum in orange-red plates; it melts at 158—159°, and is insoluble in water, but readily dissolves in organic media, and is deposited from alcohol in pale-yellow needles. On heating the amido-compound with glycerol, sulphuric acid, and orthonitrophenol, *ethylenediquinoline*, $C_9NH_6{\cdot}CH{:}CH{\cdot}C_9NH_6$ [CH : CH = 2′ : 2], is formed, but could not be obtained in crystals; it is readily soluble in alcohol, benzene, and chloroform. The *salts* and *platinochloride* are amorphous. The *methiodide* crystallises from methyl alcohol in golden-yellow needles, melts at 225—226°, and is insoluble in benzene, but readily dissolves in hot water.

No dimethyl iodide could be prepared. A *bromo*-additive compound is formed by the action of bromine on the methiodide in chloroform solution, and is deposited from methyl alcohol in slender crystals which commence to decompose at 180—190°, and melt at 210°.

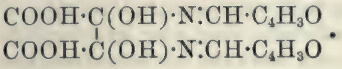
Ethylenequinolinequinaldine, $C_9NH_6{\cdot}CH{:}CH{\cdot}C_9NH_5Me$ [CH = 2′; CH:Me = 2 : 2′], is prepared by the action of paraldehyde on amidobenzylidenequinaldine, and forms a yellow, plastic mass readily soluble in alcohol, benzene, or ether. The *nitrite* crystallises from water in stellate groups of reddish-yellow needles which commence to decompose at 125°, and melt at 135—136°. The *hydrochloride*, *nitrate*, *sulphate*, *picrate*, *and platinochloride* are all amorphous and readily soluble. J. B. T.

β-Pyrazoledicarboxylic Acids. By MAQUENNE (*Compt. rend.*, **111**, 740—743).—Dinitrotartaric acid not only acts on formaldehyde and acetaldehyde in presence of ammonia, but the reaction is general, and the author has prepared in this way a number of β-pyrazoledicarboxylic acids from the corresponding aldehydes. They are all only slightly soluble even in boiling water, and are almost insoluble in alcohol, but dissolve very readily in alkaline solutions, and yield mono-metallic salts which are neutral and crystallisable. Methyl-, ethyl-, and isopropyl-glyoxalinedicarboxylic acids crystallise with 1 mol. H_2O in brilliant, acicular prisms; the others form crystalline, anhydrous powders. Isobutylglyoxalinedicarboxylic acid and its alkaline salts have a sweet taste, but this property is wanting in the neighbouring homologues.

All the glyoxalinedicarboxylic acids decompose at about 300°, and yield carbonic anhydride and glyoxalines or β-pyrazoles, the decomposition being almost quantitative. This constitutes the best method for the preparation of glyoxalines. Many glyoxalines were prepared in this way, and the hexyl-glyoxaline was found to melt at 45—46°, and not at 84° as stated by Radziszewski.

2-*Phenyl-β-pyrazole* is solid, very slightly soluble in water or in warm benzene (from which it crystallises in lamellæ), but easily soluble in alcohol. It melts at 148°, and boils at about 340° (uncorr.), which distinguishes it from the isomeric 1-phenyl-α-pyrazole described by Knorr, which melts at 11°, and boils at 246·5°. The normal oxalate crystallises from aqueous solutions in anhydrous needles; the platinochloride is anhydrous, and forms orange, microscopic crystals almost insoluble in cold water.

Difurfuramidodihydroxytartaric acid.—Furfuraldehyde does not act on dinitrotartaric acid in the same way as other aldehydes. When the aldehyde and acid in molecular proportion react in presence of excess of ammonia, a crystalline precipitate forms, and can be purified by solution in ammonia and reprecipitation with hydrochloric acid. It resembles the glyoxalinedicarboxylic acids in appearance, but has not their general properties, and yields no glyoxaline when distilled. The ammonium salt has the composition $C_{14}H_{10}N_2O_8(NH_4)_2 + 2H_2O$. The acid has the composition $C_{14}H_{12}N_2O_8$, is formed by the union of 2 molecules of furfuraldehyde with 1 molecule of tartaric acid, and probably has the constitution



$$\begin{array}{l}COOH\cdot C(OH)\cdot N\colon CH\cdot C_4H_3O \\ \quad\quad\quad\;\; | \\ COOH\cdot C(OH)\cdot N\colon CH\cdot C_4H_3O\end{array}.$$

C. H. B.

Caffeïdine. By E. SCHMIDT and M. WERNECKE (*Arch. Pharm.*, **228**, 516—543).—Caffeïdine sulphate was prepared by boiling caffeïne with barium hydroxide (Strecker's method) for half an hour only; white, needle-shaped crystals were finally obtained which are easily soluble in water, much less soluble in alcohol. By treating the sulphate with barium hydroxide, a little water, and chloroform, the free base is obtained as a solid, crystalline mass with a neutral reaction; it melts at about 94°. The free base readily decomposes with the formation of ammonia, methylamine, and cholestrophane. *Caffeïdine hydriodide*, obtained by neutralising the free base with dilute hydriodic acid, forms white, tabular, anhydrous needles, easily soluble in hot water, somewhat less soluble in hot alcohol, insoluble in chloroform. *Caffeïdine hydrochloride*, obtained by treating the hydriodide in aqueous solution with silver chloride, forms long, thin, somewhat hygroscopic needles. *Caffeïdine nitrate*, prepared by precipitating the hydriodide solution with silver nitrate, forms large, white, strongly hygroscopic needles. Caffeïdine sulphate, when treated with nitric acid, yields chlolestrophane, ammonia, methylamine, and carbonic anhydride; but no ammonia is formed if the mixture is heated for a long time.

Oxidation of the sulphate with potassium dichromate and sulphuric acid yields the same products, and not diethyloxamide as found by Maly and Andreasch, excepting when the mixture is heated for some time. Oxidation with bromine gives the same compounds, as does also treatment with potassium chlorate and hydrochloric acid. Fuming hydrochloric acid completely decomposes caffeïdine sulphate at 150° with the formation of carbonic anhydride, formic acid, ammonia, methylamine, and sarcosine (compare Abstr., 1888, 69). J. T.

Derivatives of Morphine. By W. DANCKWORTT (*Arch. Pharm.*, **228**, 572—595).—Morphine, when heated with excess of acetic chloride, yields diacetylmorphine (the tetracetylmorphine of Wright). This compound, when boiled with water loses only one acetyl group, and α-monoacetylmorphine is formed; by the addition of hydrochloric acid, this can easily be obtained as the sparingly soluble hydrochloride. The β-monoacetyl (β-diacetyl of Wright) compound was prepared by Becket and Wright's method (this Journ., 1874, 1033), but their γ-compound was not obtained. The stability of morphine was not found to be increased by the entrance of the acetyl group, as shown by the reaction of diacetylmorphine with dilute nitric acid and with bromine, although this is known to be the case with codeïne and the methyl group. Anhydrous morphine, when heated at 100—110° with twice the amount of benzoic chloride, yielded dibenzoylmorphine, which supports the view that the morphine molecule contains only two hydroxyl groups. Polstorff's tribenzoylmorphine could not be detected. By heating oxydimorphine with acetic chloride, tetracetyloxydimorphine is obtained, which doubtless is identical with Hesse's diacetylpseudomorphine, obtained by the action of acetic anhydride on pseudomorphine. The entrance of the four acetyl groups indicates that four hydroxyl groups exist intact in the oxydimorphine, and that the hydrogen atoms replaced must have been united with carbon. Apomorphine, when treated with excess of acetic chloride, yields monacetylapomorphine; hence only one hydroxyl group is present in apomorphine, the second hydroxyl group of morphine during its conversion into apomorphine going to form a molecule of water. Probably the alcoholic hydroxyl of morphine is the one expelled, the phenyl hydroxl having greater stability. This, to some extent, will account for the chemical and physiological difference between morphine and apomorphine. J. T.

Cinchonamine. By ARNAUD (*Ann. Chim. Phys.* [6], **19**, 93—131) See this vol., p. 362.

Berberine and Hydroberberine. By R. GAZE (*Arch. Pharm.*, **228**, 604—662; compare Abstr., 1890, 1012).—Chloroformberberine, dissolved in a little hot chloroform and treated with alcohol, quickly gives long, prismatic crystals of *dichloroformberberine*,

$$C_{20}H_{17}NO_4,CHCl_3+CHCl_3.$$

The crystals soon lose their transparency when preserved, and decompose with evolution of chloroform when warmed. J. T.

Ecgonine. By U. Mussi (*Chem. Centr.*, 1890, ii, 516—517; from *L'Orosi*, **13**, 152—158).—The author has already (*L'Orosi*, **11**, 270—277) recommended that, since the direct detection of cocaïne is difficult, the products of its decomposition should be sought for in toxicological investigations. With this object, he has examined the behaviour of ecgonine with various reagents. According to Einhorn this alkaloïd is *methyltetrahydropyridyl-β-hydroxypropionic acid*,

$$C_5NH_7Me{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH,$$

and reacts both as a base and an acid; it crystallises in colourless, lustrous, monoclinic prisms with 1 mol. H_2O, which is lost at 120—130°. It is very readily soluble in water, less easily in absolute alcohol, insoluble in ether, chloroform, and carbon bisulphide. Its solutions are neutral, and have a somewhat bitter taste. It melts at 198° with partial decomposition. With phosphomolybdic acid, it forms a yellow precipitate; with somewhat concentrated gold chloride solution, a yellow, amorphous precipitate; with platinic chloride in dilute alcoholic solution a red-brown, crystalline precipitate, $(C_9H_{15}NO_3)_2,H_2PtCl_6$, which is readily soluble in water, and loses hydrogen chloride when heated, forming the salt $(C_9H_{15}NO_3)_2PtCl_4$. With stannic chloride, mercuric chloride, tannin, and picric acid, it forms no precipitates which distinguish it from cocaïne. Especially is the reaction with Wenzell's reagent (200 parts of sulphuric acid and 1 part of potassium permanganate) delicate, a clear wine-red coloration being formed which disappears only after some time.

In an experiment with a rabbit, 1·26 grams of ecgonine per kilo. of live weight was found to be fatal. After 48 hours, the entrails were divided into five parts, and each part digested several times at 60° with twice its weight of alcohol, and the extract concentrated nearly to dryness. The residue was taken up with water, and shaken several times with ether in order to extract fatty substances. The aqueous solution was precipitated with basic lead acetate, filtered, the lead removed as sulphide, the liquid again filtered, evaporated to dryness, and the residue finally extracted with a little absolute alcohol, in which the ecgonine exists as acetate and was readily detected. The alkaloïd was found in the heart, blood, lungs, liver, brain, and spinal cord.

Ecgonine Salts.—$(C_9H_{15}NO_3)_2Mg + 3\frac{1}{2}H_2O$, very hygroscopic plates, soluble in water and alcohol, insoluble in ether, melting at 190°. $(C_9H_{15}NO_3)_2Ca$ is soluble in water and alcohol, insoluble in ether. $C_9H_{15}NO_3Ag$, orange-coloured, decomposing readily when exposed to the light. *Ecgonine acetate*, $C_9H_{15}NO_3,C_2H_4O_2 + 2\frac{1}{2}H_2O$, needle-like, hygroscopic crystals, melting at 196°, very soluble in water and alcohol, insoluble in ether. J. W. L.

New Alkaloïd from Chrysanthemum cinerariæfolium. By F. Marino Zuco (*Chem. Centr.*, 1890, ii, 560—561; *Rend. Acad. Lincei*, **6**, i, 571—575).—In addition to the two substances, the one a paraffin and the other a homologue of cholesterol, which the author has already described (Abstr., 1890, 757), he has further separated a glucoside and an alkaloïd from the flowers of *Chrysanthemum cinerariæfolium.* Both were obtained from the blossoms by extraction with ether. The glucoside is crystalline, but could not be obtained in sufficient quantity for proper investigation. The alkaloïd, named *chrysanthemine* by the author, is readily soluble in water, and its solution may be concentrated on the water-bath without decomposition, whereby the base is obtained as a colourless syrup. The majority of its salts are soluble in water, alcohol, and ether, and are crystalline. The most characteristic of these is the aurochloride, which crystallises in small, golden-yellow needles, very soluble in hot water, sparingly so in cold water, readily in alcohol, and moderately soluble in a mixture of alcohol and ether (1 : 1). Potassium bismuth iodide forms a yellow precipitate with it, and potassium mercury iodide forms a yellowish-white precipitate. Platinum chloride, tannin, and picric and phosphotungstic acids do not form precipitates with it. The analysis of the aurochloride agrees with the formula $C_{14}H_{30}O_3N_2,2AuCl_4$, according to which the formula of the hydrochloride would be $C_{14}H_{30}O_3N_2Cl_2$. J. W. L.

Ulexine and Cytisine. By A. W. GERRARD and W. H. SYMONS (*Pharm. J.* [3], **20**, 1017).—The authors enumerate the following differences between ulexine, the alkaloïd of *Ulex europæus*, already described by them, and cytisine, the alkaloïd of *C. laburnum*, which has been supposed to closely resemble, or be identical with, the former. Ulexine has the formula $\frac{1}{2}(C_{22}H_{28}N_4O_2)$; is very hygroscopic, cannot be sublimed, even in a vacuum, without decomposition, and dissolves readily in chloroform. Cytisine has the formula $C_{20}H_{27}N_3O$, is permanent in air, sublimes completely, forming splendid crystals, and is almost insoluble in chloroform. The formula given for ulexine differs only by CO from that of nicotine, and by H_2O from that of pilocarpine, and there is a certain likeness in the physiological action of these alkaloïds, notwithstanding the differences in their chemical behaviour. Some progressions of properties are traced in the alkaloïds from leguminous plants arranged according to the percentage of carbon, thus :—sparteïne, pyridine, nicotine, cytisine, ulexine, eserine, and pilocarpine; in this series, the physiological activity becomes more powerful, and the instability greater with decrease in the percentage of carbon. R. R.

Alkaloïds and other Active Principles from Plants Growing in the Dutch Indies.—By M. GRESHOFF (*Ber.*, **23**, 3537—3550).—I. *Carpaïne, the Alkaloïd of Carica papaya*, L.—The leaves of the papaya (*Carica papaya*, L.) contain, in addition to the caricine and papaïne discovered by Wurtz and Peckolt, an alkaloïd which has not previously been prepared, and for which the name *carpaïne* is proposed. The young leaves are richest in the alkaloïd, and contain about 0·25 per cent.; the sap, seeds, and roots only contain traces. Carpaïne is readily soluble in alcohol, chloroform, and ether, the freshly precipitated compound being more readily taken up by the latter solvent than when crystallised, a fact which is made use of in isolating the alkaloïd. It is completely separated from solutions of its salts by sodium carbonate solution, but is insoluble in potash, and cannot be extracted from acid solution. It gives precipitates with Mayer's solution, iodine, phosphomolybdic acid, picric acid, gold chloride, tannin, potassium thiocyanate, &c., melts at 115°, and sublimes partly without decomposition. Its *hydrochloride* crystallises in beautiful, lustrous needles, and is readily soluble in water. The base, even when dissolved in 100,000 parts of water, has a bitter taste, and is only poisonous in large doses, but small quantities readily kill smaller animals, the action taking place on the heart.

II. *Investigation of Indian Leguminous Plants.*—The plant known as *Derris* (*Pongamia*) *elliptica*, Benth., is largely used in Java in fishing, and appears also to be a constituent of the Borneo arrow-poison. It has an exceedingly poisonous action on fish, a decoction of the roots being fatal even when diluted with 300,000 parts of water. The only active constituent isolated is a resinous substance termed *derrid*, which does not contain nitrogen and is not a glucoside; it readily dissolves in alcohol, ether, chloroform, and amyl alcohol, but is very sparingly soluble in water and potash solution. On fusion with potash, it yields salicylic and protocatechuic acids. It occurs almost entirely in the cortex of the root, but has not yet been obtained pure. Its alcoholic solution has a slightly acid reaction, and a sharp aromatic taste, causing a partial insensibility of the tongue, which remains for hours. A solution of 1 part in 5 millions is almost instantly fatal to fish. A very similar compound is found in the seeds of *Pachyrhizus angulatus*, Rich., a decoction of which is quickly fatal in a dilution of 1 : 125,000. It is probably identical with derrid, but until this has been experimentally proved it may be distinguished as pachyrhizid. It is very readily prepared from *Pachyrhizus*, which occurs in all tropical countries, as the tannin compounds, usually so difficult to separate, are not found in this plant. The seeds also contain a non-poisonous, crystalline compound, which is readily soluble in alcohol, and has at 30° the consistence of butter.

The plant *Sophora tomentosa*, L., formerly renowned as a medicine ("*Anticholerica Rumphii*"), contains a poisonous alkaloïd, soluble in ether, which is contained in largest quantity in the seeds. Alkaloïds have previously been found in *S. speciosa* and *S. angustifolia*, but have not been closely investigated.

The cortex of *Erythrina* (*Stenotropis*) *Broteroï*, Hassk., contains considerable quantities of an alkaloïd, which may be readily isolated by Stas's method, and is easily soluble in ether. Its sulphate may be obtained in crystals from concentrated aqueous solution. It gives precipitates with many metallic salts and with the usual alkaloïd reagents; it is a fairly strong poison, being fatal to fowls in doses of 0·025 gram. A poisonous alkaloïd likewise exists in *Erythrina* (*Hypaphorus*) *subumbrans*, Hassk., and is best isolated as a metallic double compound.

The leaves of different kinds of cassia are employed in Java as a remedy for herpes; they contain a glucoside which yields chrysophanic acid as a product of hydrolysis.

The leaves of *Crotolaria retusa*, L., contain considerable quantities of indican; the seeds contain an alkaloïd, which is found in larger quantities in the seeds and leaves of *C. striata*, L. The base is a strong poison, and is probably closely related to the known alkaloïds of other Genisteæ, such as *Cytisus*, *Ulex*, *Spartium*, and *Lupinus*.

The seeds of *Millettia atropurpurea*, Benth., contain a poisonous glucoside, the chemical and toxicological properties of which closely resemble those of saponin. The plant is also employed for poisoning fish. The cortex of *Acacia tenerrima*, Jungh., contains a bitter, poisonous alkaloïd, readily soluble in ether and chloroform. No alkaloïd has previously been found in an acacia. The leaves of *Albizzia saponaria*, Bl., contain cathartic acid, whilst the leaves and cortex contain saponin in quantity.

The cortex of *Pithecolobium bigeminum*, Mart., contains 0·8 per cent. of a non-volatile, amorphous alkaloïd, which forms crystalline salts, and separates as a heavy, yellow oil on the addition of alkalis to solutions of the latter. With 100 parts of water, it forms a turbid liquid, which on warming assumes the appearance of milk, but becomes clear on the addition of an acid. The solutions have a burning taste, and give the usual alkaloïd reactions. It has a strong corrosive action on the skin, and is fatal to fish in a dilution of 1 : 400,000. The same compound appears also to occur in *P. saman*, Benth.

III. *Apocyneæ containing Alkaloïds, occurring in the Dutch Indies.*—The leaves, cortex, and seeds of *Melodinus lævigatus*, Bl., all contain a poisonous alkaloïd, which is present in the largest quantity in the seeds (0·8—1·0 per cent.). It is decomposed by dilute hydrochloric acid, but is not a glucoside, and gives the ordinary alkaloïd reactions in very dilute solutions, and with feeble oxidising agents in sulphuric acid solutions gives a greenish coloration, which then becomes deep blue and finally orange.

Leuconotis eugenifolia, Dec., yields a poisonous, crystalline alkaloïd which is readily soluble in ether, and shows the general reactions of the alkaloïds, but gives no colour reactions. The cortex of *Rauwolfia canescens*, W., yields an alkaloïd which gives a beautiful, blood-red coloration with nitric acid. *Rauwolfia* (*Ophioxylon*) *serpentina* and *trifoliata*, which is highly prized in Java as a drug, also contains a crystalline alkaloïd which gives the same reaction with nitric acid, and its presence may be easily recognised microscopically in the various parts of the plant by this reaction. The substance recently described as ophioxylin is identical with Dulong's plumbagin, the error being caused by a confusion between *Ophioxylon serpentinum*, L., and *Plumbago rosea*, L., which, though very different plants, are both termed "Poeleh Pandak" in Java. The above alkaloïd also occurs in *Rauwolfia* (*Cyrtosiphonia*) *spectabilis* and *madurensis*. All these species of *Rauwolfia* contain a brown substance also; this likewise appears to be an alkaloïd, and yields a beautiful, blue, fluorescent solution in ether. It is constituent of many *Apocyneæ*.

The cortex of *Hunteria corymbosa*, Roxb., contains 0·3 per cent. of a crystalline alkaloïd, which also forms crystalline salts, and gives a beautiful violet coloration with Erdmann's and Fröhde's reagents. It is a strong poison, and has a sharp, burning taste, even when diluted to 1 : 10,000. The cortex of *Pseudochrosia glomerata*, Bl., also contains a poisonous, crystalline alkaloïd, and the above fluorescent compound.

The cortices of *Ochrosia* (*Lactaria*) *acuminata*, *Ackeringae*, and *Coccinea* are rich in alkaloïd constituents. Three products have been isolated, namely, a colourless, crystalline alkaloïd soluble in ether, which is moderately poisonous, an alkaloïd insoluble in ether but soluble in amyl alcohol, which is best isolated as the mercurochloride, and also the above-mentioned fluorescent compound. These substances also occur in the seeds and the sap. The cortex of the stem of *Ochrosia (Bleekaria) kalocarpa* contains 1·2 per cent. of alkaloïds.

The seeds of *Kopsia flavida*, Bl., contain no less than 1·85 per cent. of a homogeneous alkaloïd, which is soluble in ether and readily prepared pure and crystalline; it likewise occurs in *Kopsia arborea*, Bl., the leaves of which contain in addition a fluorescent substance. *Kopsia (Calpicarpum) Roxburghii* yields quite a different alkaloïd, which causes tetanus. The seeds and leaves of *Kopsia (Calpicarpum) albiflorum* contain an alkaloïd, as also do *Vinca rosea*, L., and *Alstonea (Blaberopus) villosa.*

Voacanga (Orchipeda) fœtida yields a bitter alkaloïd readily soluble in ether, and the fluorescent compound already frequently mentioned. *Tabernæmontana sphærocarpa*, Bl., also contains an alkaloïd, and a wax-like compound, which is free from nitrogen and melts at 185°. Alkaloïds are also present in *Rhyncodia (Cercocoma) macrantha* and in *Chonemorpha macrophylla*, Don, which is of interest, inasmuch as these species both belong to the *Echitidiæ*, the other members of which are free from alkaloïds.

IV. *Cerbera odollam*, Hamilt.—The sap, leaves, and cortex of this plant have no toxicological action, but the seed kernel contains, in addition to a non-poisonous fatty oil, the compound *cerberin*, which has a poisonous action on the heart. It resembles thevetin, thevetosin, and tanghinin, but is identical with none of them. It most nearly resembles the last-named substance, which is obtained from *Tanghinia venenifera*, Poir., the "test-plant" of Madagascar. Cerberin is free from nitrogen and crystallises well, and although decomposed by acids, is not a glucoside. It is insoluble in water, but dissolves readily in alcohol, chloroform, acetic acid, and 80 per cent. ether, and melts at 165°. It gives a violet coloration with sulphuric acid, has a sharp, burning but not bitter taste, and is very poisonous. The seeds contain another very poisonous substance, which is readily soluble in water, alcohol, and amyl alcohol, but insoluble in chloroform, for which the name odollin is proposed. It is not precipitated by lead acetate, and gives the same colour reaction with sulphuric acid as cerberin.

V. *Laurotetanine, the Active Constituent of certain Lauraceæ.*—Many of the Javan varieties of Lauraceæ contain, in addition to other not yet clearly defined bases, a crystalline alkaloïd termed *laurotetanine*, which has a strong tetanic action on animals. It is contained in quantity in the cortex of the stem of *Litsæa chrysocoma*, Bl., and is sparingly soluble in ether, more readily in chloroform. It is precipitated by sodium carbonate from solutions of its salts, but readily redissolves in an excess of potash or soda, and is precipitated by the usual alkaloïd reagents. The freshly prepared alkaloïd commences to crystallise after some days in stellate groups of needles; it gives a dark indigo-blue coloration with Erdmann's reagent, a pale rose-red with pure sulphuric acid, and a reddish-brown with nitric acid. A base which seems to be identical with laurotetanine is also found in the varieties of *Tetranthera*, in *Notaphœbe*, Bl., *Aperula*, Bl., and *Actinodaphne*, Nees. It is possible, also, that laurotetanine is identical with the alkaloïd discovered in 1886 by Eykmann in *Haasia squarrosa*, Z. et M., as the author has also found it in *H. firma*, Bl.

Hernandia sonora, L., and *H. ovigera*, L., both yield an alkaloïd closely resembling the bebeerine obtained from *Nectandra*, whilst *Illigera pulchra*, Bl., contains laurotetanine.

VI. *The Distribution of Hydrocyanic Acid in the Vegetable Kingdom.*—The leaves of *Gymnema latifolium*, Wall, an Indian *Asclepiadea*, contain large quantities of amygdalin, which can, however, only be obtained in the amorphous condition. The leaves do not contain any enzyme, and may, therefore, be distilled with water or dilute sulphuric acid without any hydrocyanic acid or benzaldehyde passing over. On the addition of emulsin, hydrolysis readily takes place.

The fresh bark of many Javan forest trees gives off an odour of bitter almond oil. It was found that *Pygium parviflorum*, T. et B., and *P. latifolium*, Miq., both contain amygdalin, which on botanical grounds was not improbable, as the species *Pygium* is closely related to *Amygdalus*.

When the fruit of certain Javan Aroïdes (the genera *Lasia* and *Cyrtosperma*) is cut, a strong odour of hydrocyanic acid is observed, and it was found on investigation that it is present in the free state. It also occurs in the leaves of these plants. It is found, however, in much larger quantity in a Javan tree known as *Pangium edule*, Reinw., the seeds of which, after cooking in a certain manner, are looked on by the Malays as a valuable food. If this cooking is insufficient, the seeds are a frightful poison, and are used in Java for killing fish and insects. It was found on investigation that all parts of the tree contain free hydrocyanic acid. Thus the leaves, on distillation, yielded 0·34 per cent. which is equal to 1 per cent. on the dried leaves; in the other parts the proportion, although less, is still considerable. The amount of hydrocyanic acid is not constant, old *Pangium* leaves having been examined which only contained 0·045 per cent.

The leaves and seeds of the *Pangium* contain a substance which reduces ammoniacal silver solution and Fehling's solution in the cold, and whose solutions become dark-coloured in the air. Although no crystalline compound could be obtained with phenylhydrazine, it is probably a sugar, with which the hydrocyanic acid forms an unstable compound. The seeds, which are originally white, gradually become dark, the hydrocyanic acid disappearing at the same time.

The only poisonous constituent of the genus *Hydnocarpus* is also hydrocyanic acid. The fatty oils of certain species of *Hydnocarpus* are used externally in skin diseases, their value being possibly due to the antiseptic action of hydrocyanic acid. H. G. C.

Coagulation. Preparation of Soluble Caseïn. By A. Béchamp (*Bull. Soc. Chim.* [3], **4**, 181—186).—The author takes exception to the undefined meaning of the word coagulation, as applied to the separation of the proteïds from milk, under varying conditions, and describes the following method for preparing a soluble caseïn which is not coagulable by heat. Pure acetic acid is dropped into milk just drawn from the cow or goat, until the milk turns litmus-paper a pale pink, and the coagulum which soon separates out is collected, and, after drying by a filter pump, is treated with ether to remove fat; it is then suspended in a volume of water equal to that of the original milk, and containing ammonium carbonate, and the mixture is filtered. To the limpid solution thus obtained, acetic acid is added exactly sufficient to precipitate the caseïn, which, by a repetition of the above treatment, is obtained pure.

The rotatory power of this substance in ammoniacal solution is $[\alpha] = -130°$. It is soluble in water, 1 litre dissolving, on agitation for 56 hours, 1·005 grams, and the rotatory power of this solution is $[\alpha]_j = -117°$. A paste of caseïn and water softens at 70—80°, and appears to be quite soft at 90°, the water separated from this product contains 2·37 grams caseïn per litre; and, although the paste hardens on cooling, it is soluble in ammonium carbonate solution, and on precipitation by acetic acid, manifests its original properties. Caseïn behaves like a feeble acid, its solutions redden litmus, and it forms compounds with the alkali metals and with ammonia which also redden litmus, and are neither precipitated by carbonic anhydride, nor by alcohol, nor by heating. Calcium caseïnate behaves like calcium saccharate in becoming turbid on ebullition, and in the disappearance of the turbidity on cooling. The author ascribes the incorrect results hitherto obtained to the practice of boiling the milk before adding the acid, by which lactalbumin and galactozymase are precipitated as well. These substances are separated from the whey left after removal of the caseïn, by adding to it alcohol of 95° as long as a precipitate falls; the latter is collected and washed with alcohol of 80°, to remove lactose, and is then air-dried and suspended in water; after some time, it is filtered, and the precipitate is washed with water as long as the washings give a precipitate with alcohol.

Lactozymase is separated from the filtrate by the addition of alcohol and a trace of sodium acetate; it is soluble in water, and has the power of determining the dissolution of starch without subsequent hydrolysis; it is coagulable by heat and then loses this property.

Lactalbumin is obtained by dissolving the residue in dilute ammonium carbonate solution and precipitating by acetic acid; when it is suspended in water and heated to 100°, it contracts in volume and is no longer soluble in ammonium carbonate solution.

T. G. N.

Proteïds of Milk. By W. D. HALLIBURTON (*J. Physiol.*, **11**, 448—463).—Attention is drawn in this paper to the following points:—

(1.) The principal proteïd in milk precipitable by saturation with certain neutral salts or by acetic acid, should be called *caseïnogen*. It may be most satisfactorily prepared free from impurities by a combination of the two methods just mentioned. The term *caseïn* should be restricted to the curd formed from caseïnogen by the action of rennet.

(2.) In the classification of proteïds, caseïn should be grouped with other insoluble proteïds, like fibrin and gluten, formed by ferment activity from pre-existing more soluble proteïds. Caseïnogen should be classified in a new group, made to include it and whey-proteïd. These are very similar to the globulins; the chief difference being that their solutions are not coagulated by heat like the globulins, but only rendered opalescent. This opalescence, if the heating has not been continued too long, disappears on cooling.

(3.) Lactalbumin is very similar in its properties to serum-albumin. Not only does it differ, however, from serum-albumin in its specific rotatory power, as has previously been shown, but in its behaviour on heat-coagulation, and in precipitability by certain neutral salts.

(4.) Caseïnogen and lactalbumin are the only proteïds contained in milk. The proteïd described as lactoglobulin does not exist; it is owing to the error of not recognising that the two salts, sodium chloride and magnesium sulphate, when both present to saturation, precipitate albumin, that this proteïd has been supposed to exist. The proteïds variously called lactoproteïn, peptone, and hemialbumose, do not exist in milk. This mistake has also arisen from faulty methods of analysis.

(5.) The proteïd called whey-proteïd, which passes into solution simultaneously with the formation of the rennet curd, is not of the peptone or proteose class, but should be included with caseïnogen in a new class of proteïds allied to the globulins. It differs from caseïnogen in not being convertible into caseïn.

(6.) When milk turns sour owing to the lactic acid fermentation, primary proteoses, chiefly proto-proteose, are developed.

W. D. H.

Note.—Hammarsten, in his text-book of Physiological Chemistry recently published, also recognises that caseïnogen should not be grouped with alkali albuminates, as has hitherto been the case. He classifies it with the nucleo-albumins. W. D. H.

Action of Lime Salts on Caseïn and on Milk. By S. Ringer (*J. Physiol.*, **11**, 464—477).—Caseïn, prepared by adding commercial rennet to milk, was found to be freely soluble in lime-water; on the addition of calcium chloride to this solution, a compound of caseïn is formed which is more soluble in cold than in hot solutions. A few drops of calcium chloride solution does not cause precipitation at all in the cold, but, on warming, a precipitate forms closely resembling a rennet curd, and, like it, it contracts, squeezing out a whey. On cooling this, however, it completely redissolves. Larger quantities of calcium chloride cause a precipitate in the cold, which increases when the mixture is heated. Sodium chloride in 0·5, 1, and 2 per cent. solutions does not modify this action; whilst lactose greatly aids the action of the calcium salt.

Similar experiments were then tried with milk. Calcium chloride causes no curdling of milk at the atmospheric temperature (10° to 15°), in this respect differing strikingly from solutions of caseïn in lime-water, from which 1 to 3 drops of a 10 per cent. solution of calcium chloride precipitates abundance of curd or sets the fluid to a jelly. Calcium chloride, however, abundantly precipitates curd from milk with the assistance of heat, the smaller the quantity of calcium chloride the higher the temperature required. Slight acidity favours, sodium chloride and to a less extent potassium chloride and magnesium sulphate hinder this action of calcium chloride. Hence milk differs from caseïn dissolved in lime-water in respect to the action of sodium chloride. Lactose, which greatly favours the clotting of a lime-water solution of caseïn by calcium chloride, does not influence the clotting of caseïnogen as contained in milk.

Calcium chloride solution does not clot milk which has been previously boiled and then cooled. Hence it is evident that the high temperature necessary in the experiments does not alter the caseïnogen, and thus enable calcium chloride to precipitate it, but that the high temperature is necessary to enable calcium chloride to precipitate (combine with) caseïnogen.

Caseïnogen can be prepared as follows :—10 per cent. acetic acid is added to milk; the resulting precipitate is washed with distilled water until the washings are neutral and free from calcium salts. The curd is rubbed in a mortar with calcium carbonate, and distilled water added; the caseïnogen rapidly dissolves, and the butter separates and floats on the top. After some hours, the milky fluid below is siphoned off. Rennet clots this solution if a small quantity of calcium chloride is added, but not without. The rennet used (Crosse and Blackwell's) contains a good deal of calcium, but this is either insufficient, or in inappropriate form. But, although the fluid does not clot, the caseïnogen is converted into caseïn, which remains in solution, and this is at once deposited on adding calcium chloride, each drop producing an abundant deposit, insoluble in solution of sodium chloride. Sodium and potassium salts antagonise the clotting of caseïnogen solutions, as in the case of milk; in the former case they lessen, too, the subsequent contraction of the clot. If phosphoric acid is essential, as Hammarsten stated, the minute quantity present in the preparation of rennet must have sufficed, as none was added in the experiments.

Calcium chloride solution precipitated caseïnogen from its solution without the assistance of rennet; only larger quantities are necessary than is the case with solutions of caseïn. Lactose has no effect on the precipitation of caseïnogen by calcium chloride. Corroborative results were obtained with caseïnogen precipitated by saturating milk with sodium chloride.

Among further differences between caseïnogen and caseïn, the two following may be noted :—

(1.) Caseïn is insoluble in a fairly strong solution of sodium chloride; caseïnogen is soluble.

(2.) Caseïnogen precipitated by acetic acid and mixed in a mortar with calcium carbonate is freely soluble in distilled water. Caseïn similarly treated is insoluble.

The process of ordinary curdling in milk by rennet is believed to consist of two parts :—

(1.) The change from caseïnogen to caseïn, produced by the ferment.

(2.) The combination of the caseïn so formed with a lime salt, the precipitation of this compound being assisted by the lactose, but opposed by the sodium and potassium salts of the milk. These salts also lessen the degree of contraction of the clot, and hence a bulky clot instead of a compact one is obtained. W. D. H.

Digestion Products of Gluten-caseïn. By R. H. Chittenden and E. E. Smith (*J. Physiol.*, **11**, 410—434).—The methods of investigation are essentially the same as those adopted in the similar researches of Kühne, Chittenden, and others. Although it is questionable whether gluten exists in fresh wheat grains, it is nevertheless true that gluten is formed whenever wheat flour is mixed with water, and of this gluten the insoluble portion, characterised by Ritthausen as gluten-caseïn, is the most important constituent. The percentage composition of this material (the average of analyses of seven preparations) may be contrasted with the numbers obtained by Ritthausen, and with the percentage composition of the caseïn of milk, as in the following table :—

	Gluten-caseïn.		Caseïn of milk.	
	Chittenden and Smith.	Ritthausen.	Chittenden and Painter.	Hammarsten.
C	52·87	52·94	53·30	52·96
H..... ...	6·99	7·04	7·07	7·05
N.........	15·86	17·14	15·91	15·65
S	1·17	0·19	0·82	0 72

On subjecting gluten-caseïn to artificial gastric digestion, it was found that solution occurs very slowly, probably the result of the prolonged washing with alcohol in its preparation. Artificial pancreatic digestion also proceeds slowly, but there is a more abundant formation of true peptone, as compared with primary cleavage products (proteoses), than is the case with gastric digestion. The soluble products formed in each case bear essentially the same relation to the parent substance as the albumoses of albumin or fibrin do to the parent proteïd. There are slight differences in minor reactions, but no essential difference in the general character of the products formed in this case, at least between the animal and vegetable proteïd. Both yield by the action of pepsin acid a proportionately large amount of proteoses and a small amount of true peptone. The gluten-caseoses, both in composition and reactions, show the ordinary proteose characteristics, and the composition of the individual products (proto-, hetero-, and deutero-gluten-caseose), as indicated by the gradually diminished percentage of carbon, suggests that they are formed by a gradual process of hydration. W. D. H.

Crystalline Vitellin and Vitelloses. By R. H. Chittenden and J. A. Hartwell (*J. Physiol.*, **11**, 435—447).—This research, carried out on the same lines as the preceding, confirms in the main the work of Neumeister (Abstr., 1887, 286); it was judged advisable to repeat the experiments, as vitellin (crystallised in this research from extracts of squash or pumpkin seeds by Drechsel and Grubler's method) is the purest proteïd obtainable. Scarcity of material prevented the investigation of many points, but the general conclusion is that, in gastric digestion, the changes, as in the case of other proteïds, are hydrolytic in nature; proto-proteose, deutero-proteose, and peptone resulting from a series of gradual hydrations, as indicated by the gradually diminished percentage of carbon. The amount of hetero-vitellose formed was small.

Attention was particularly directed to the percentage composition of the products, and the following table collects a few of the averages obtained:—

	C.	H.	N.
Vitellin	51·60	6·97	18·80
Proto-vitellose	51·52	6·98	18·67
Deutero-vitellose (1)	50 42	6·74	18·43
„ „ (2)	49 27	6·70	18·78

The results agree very closely with those previously obtained with the globulin body, myosin, the composition of the myosinoses bearing almost exactly the same relationship to myosin as the vitelloses do to the crystallised globulin. A single experiment on tryptic digestion showed nothing noteworthy. W. D. H.

Crystallisation of Hæmoglobin. By S. M. Copeman (*J. Physiol.*, **11**, 401—409).—This is a full account of experiments a preliminary notice of which has already appeared (Abstr., 1889, 1092). Among new points noticed, is the fact that some crystals of human hæmoglobin were after the lapse of some months changed into crystals of hæmochromogen. Hoppe-Seyler has previously prepared crystalline hæmochromogen (Abstr., 1889, 788).

It was found that, using the method of adding putrid serum to the blood, the hæmoglobin crystals of the squirrel obtained were not the usual hexagons, but rhombic prisms. (Compare Halliburton, Abstr., 1886, 637). W. D. H.

Compounds of Hæmoglobin with Carbonic Anhydride. By C. Bohr (*Chem. Centr.*, 1890, ii, 521; from *Centr. Physiol.*, **4**, 253—254).—As already communicated (Abstr., 1890, 1450), there are several compounds of hæmoglobin and carbonic anhydride, containing varying proportions of the latter, but showing dissociation curves which are approximately similar. The author now describes the three following:—*γ-carbohæmoglobin*, which contains about 3·0 c.c. of carbonic anhydride per gram at 18° under a pressure of 60 mm. of carbonic anhydride; *δ-carbohæmoglobin*, which contains about 6·0 c.c. of carbonic anhydride under the same conditions of temperature and pressure; *β-carbohæmoglobin*, which contains about 1·5 c.c. of carbonic anhydride per gram. If hæmoglobin is shaken with a mixture of carbonic anhydride and oxygen, both the gases are absorbed in the same manner as though each of the gases was present alone. The spectrum of these hæmoglobin compounds appear to be the same as that of oxyhæmoglobin. The author concludes that the carbonic anhydride and the oxygen combine differently and independently with the hæmoglobin, and the possibility exists that arterial blood fully charged with oxygen may, nevertheless, absorb carbonic anhydride. J. W. L.

Physiological Chemistry.

Effect of Acetic Acid on Respiratory Changes. By A. Mallèvre (*Compt. rend.*, **111**, 826—828).—Rabbits which had been subjected to tracheotomy were placed under artificial respiration, voluntary movements being prevented by injection of curarine. The products of respiration under these conditions were collected and analysed. A 3 per cent. solution of sodium acetate was introduced into the blood drop by drop, and the products of respiration were again examined. Before injection, the extreme values of the respiratory ratio CO_2/O were 1·04 and 0·77, but during injection, they sank to 0·86 and 0·69 respectively, a result due to oxidation of the sodium acetate. During injection, the blood becomes alkaline, but afterwards again becomes acid. Part, and part only, of the energy of the acetate is used with profit to the organism, and in this respect acetic acid differs from the majority of food stuffs. C. H. B.

The Specific Quantities of Oxygen in Blood. By C. Bohr (*Chem. Centr.*, 1890, ii, 521—523; from *Centr. Physiol.*, **4**, 254—257). —As already intimated (Abstr., 1890, 1450), hæmoglobin does not always absorb the same quantity of oxygen. Pursuing this investigation, the author has estimated the amounts of hæmoglobin and of oxygen in blood taken systematically from dogs, the latter estimation being made after first shaking the blood with oxygen of constant temperature and pressure. The ratio between these two quantities has been named the *specific quantity of oxygen of the blood*. This ratio varies not only with different animals, but depends also on the exterior conditions under the will of the operator, and it varies further in the different parts of one and the same animal at the same time. From these facts, it may be deduced that the oxygen present in the blood exerts a varying pressure, and that this pressure has a material regulating influence on the respiratory organs. Moreover, the variations in the pressure thus exerted occur within very small limits of time, and depend on the number of blood corpuscles which are influenced. In the author's experiments, strong anæmia was brought about when the arterial blood showed a constant and lower specific quantity of oxygen than before. A similar effect was produced by inhaling air poor in oxygen. On the other hand, suffocation produced an increase in the specific quantity of oxygen, and morphine exerted a like influence (compare preceding page). J. W. L.

Influence of Proteïd on the Digestion of Foods free from Nitrogen. By T. Rosenheim (*Pflüger's Archiv*, **46**, 422—432).—In recent researches by Kumagawa (*Virchow's Archiv*, **116**), and

Hirschfeld (Abstr., 1889, 174) on metabolism, these observers stated that equilibrium is possible on smaller quantities of proteïd food than has hitherto been considered possible. Their experiments, however, lasted for too short a time for such a sweeping conclusion to be drawn; and in the present research it is shown that in a dog, proteïd food is not only valuable in itself, but that it aids the digestion of other foods which contain no nitrogen, such as carbohydrates and fats. The fæces were examined for undigested residues of carbohydrates and fats, and it was found that these were always smaller when there was admixture of proteïd in the food; also that these residues were smaller in direct proportion to the amount of albuminous material administered.

These general results are supported by six series of analyses in which full details are given. W. D. H.

The Influence of Glycerol and Fatty Acids on Gaseous Metabolism. By I. MUNK (*Pflüger's Archiv*, **46**, 303—334).—Numerous observations have been made on the question whether glycerol and fatty acids affect gaseous metabolism in any way, and particularly if they act as proteïd-sparing or fat-sparing foods. Scheremetéeffsky (*Arbeit. physiol. Anstalt, Leipzig*, 1869, 194) stated that in rabbits the intake of oxygen and output of carbonic anhydride were correspondingly increased after two-grain doses of glycerol. Zuntz and v. Mering (*Pflüger's Archiv*, **32**, 174) pointed out errors in Scheremetéeffsky's methods and conclusions. They found the intake of oxygen practically unaltered by the intravenous injection of glycerol. Their experiments were, however, not performed on curarised animals, and it is possible that the increased discharge of carbonic anhydride observed might have been due to the muscular movements of the animals. Under these circumstances, it was judged advisable to repeat these experiments, precluding the source of error

Oxygen used.	Carbonic anhydride given out.	Respiratory quotient.	Period of observation.	Dose of glycerol.
182·6	132·3	0·72	Before injection	0·5 gr. per kilo.
176·1	134·1	0·76	During ,,	
178·6	126·7	0·71	After ,,	
267·9	193·1	0·73	Before ,,	0·65 ,, ,,
263·3	207·0	0·79	During ,,	
237·8	188·7	0·79	After ,,	
283·5	191·2	0·67	Before ,,	0·68 ,, ,,
277·5	200·8	0·72	During ,,	
288·2	202·9	0·70	After ,,	
288·4	194·3	0·67	Before ,,	1·0 ,, ,,
281·0	201·3	0·72	During ,,	
256·9	178·6	0·69	After ,,	

just alluded to, by curarisation, and to extend the research to include certain fatty acids. The apparatus used was a modification of the Zuntz-Röhrig respiration apparatus, which is fully described. The experiments were made on rabbits; and the accompanying tables of analyses are averages obtained in each case from a number of observations, each of which was for a period of 15 minutes. The glycerol was injected slowly into the jugular vein.

These experiments show that during the injection, the intake of oxygen falls slightly, and the output of carbonic anhydride increases to a small extent, thus raising the respiratory quotient; and the conclusion is drawn that glycerol when burnt in the body protects from oxidation a fraction of the body fat.

A similar series of experiments were then made, injecting sodium butyrate instead of glycerol, and again the results may be given in tabular form :—

Oxygen used.	Carbonic anhydride given out.	Respiratory quotient.	Period of observation.	Dose of butyric acid.
260·9	196·1	0·75	Before injection	0·4 gr. per kilo.
280·0	190·5	0·68	During ,,	
253·3	181·2	0·71	After ,,	
290·9	228·3	0·78	Before ,,	0·5 ,, ,,
325·2	214·6	0·66	During ,,	
299·4	230·9	0·78	After ,,	
305·3	243·4	0·79	Before ,,	0·56 ,, ,,
330·9	238·0	0·72	During ,,	
306·6	235·3	0·77	After ,,	
278·9	201·0	0·72	Before ,,	0·76 ,, ,,
297·6	197·9	0 68	During ,,	
278·1	205·2	0·73	After ,,	

These experiments show that during the injection, the intake of oxygen increases, and the output of carbonic anhydride falls slightly; the respiratory quotient therefore falls. Just as in the previous experiments with glycerol, none of the substance injected appeared in the urine; it was, therefore, burnt in the body, and thus must protect a small fraction of the body fat from oxidation. The increased intake of oxygen appears to be chiefly due to the increased frequency of the heart that the soap produces. The increased necessity for oxygen is seen when one notes that, whereas each molecule of glycerol requires 3½ mols. of oxygen for complete oxidation, a molecule of sodium butyrate requires 5 mols. of oxygen for the same purpose.

A few experiments were then made with sodium oleate; the effect of doses similar to those given of the other substances just described produced a rapid decrease of the gaseous exchanges, a weakening of the heart, then syncope and death. A dose of 0·04 gram of oleïc acid per kilo. of body weight produced no alteration; a repetition of this dose caused a diminution of the gaseous exchanges by 75 per cent. W. D. H.

Transfusion of Mixtures of Blood and Salt Solution. By J. MARSHALL (*Zeit. physiol. Chem.*, **15**, 62—70).—Transfusion of salt solution is now so often used in medical practice, that it is important we should have an accurate knowledge of the process of blood regeneration that follows this procedure. Rabbits were bled until convulsions were imminent, and then a solution of one part of defibrinated blood to nine parts of 0·6 sodium chloride solution was injected; tables are given with enumeration of blood corpuscles, and percentages of hæmoglobin before and at intervals after the operation. When regeneration was complete, the animals were killed, but in no case was anything abnormal found at the autopsy. The blood corpuscles reach the normal number in a few days, but the percentage of hæmoglobin is not normal for some days, in one experiment not until 15 days later. These results coincide closely with those of J. G. Otto (*Pflüger's Archiv*, **36**, 67), who used no injection, but simply watched the course of regeneration after hæmorrhage in rabbits. W. D. H.

Amount of Dry Residue and Fat in Arterial and Venous Blood. By F. RÖHMANN and J. MÜHSAM (*Pflüger's Archiv*, **46**, 383—397).—The statement was made by Bornstein (*Zeit. Biol.*, **13**, 133) that the dry residue and fat in venous, especially portal, blood is greater than in arterial blood. In the present research, the blood was taken direct from the circulation of the living animal (dog), and no difference in the amount of dry residue could be made out in the two varieties of blood taken from the femoral vein and carotid artery respectively. Such small differences as were observable fell within the limits of experimental error. If, however, stasis of the blood within the vessels is allowed to occur, the solid residue of venous blood rises.

After hæmorrhage, the specific gravity of the blood falls, but equally so in both arterial and venous blood.

Comparative estimations of the amount of fat showed that there was no appreciable difference between the two varieties of blood. Portal blood was, however, not investigated. W. D. H.

Alkalinity of the Blood after Large Doses of Sodium Sulphate. By J. SWIATECKI (*Zeit. physiol. Chem.*, **15**, 49—61).—C. Schmidt (*Charakt. epid. Cholera*, 1850) stated that in the algide stage of cholera the alkalinity of the blood is diminished, or it may become acid, and this observation has been, since his time, often confirmed. In order to ascertain whether this is merely dependent on excessive diarrhœa, various laxative drugs were administered by Mya and Tassinari (*Virchow's u. Hirsch Jahresb.*, 1887, i, 232), but their examination of the blood gave no positive results. In the present research, doses of sodium sulphate, sufficiently large to make the blood very concentrated owing to excessive loss of water *per rectum*, were given to dogs with the same object in view. The results obtained were—

(1.) The alkalinity of the blood increases with its density as a consequence of the drug treatment.

(2.) This occurrence can be explained by the greater transudation of acids than alkalis from the blood into the alimentary tract, in accordance with laws of osmosis.

(3.) The increase of alkalinity of the blood which follows the use of mineral waters cannot therefore be explained by a passing of basic salts into the blood from the alimentary canal. W. D. H.

New Method of Hemato-alkalimetry. Relative Alkalinity of the Blood of Vertebrates. By R. Drouin (*Compt. rend.*, **111**, 828—830).—0·5 c.c. of serum is heated with water and a drop of an alcoholic solution of phenolphthaleïn, and the alkalinity is determined by means of very dilute sulphuric acid (1 : 1000). The alkalinity is due to salts, such as sodium hydrogen phosphate, sodium hydrogen urate, &c. 0·5 c.c. of serum is treated in a closed tube with more than sufficient sodium hydroxide to neutralise all the acids, and barium chloride is added in quantity more than sufficient to precipitate all carbonates, phosphates, and urates. The liquid is rapidly filtered, and the filtrate is titrated, the sodium hydroxide that has disappeared giving the real acidity of the serum.

The estimation of water is likewise made with 0·5 c.c. of serum.

The alkalinity of the blood of the vertebrates is practically the same in the same groups, but different in different groups. It is too small to be estimated in fishes, is high in mammals, and highest in birds, increasing, in fact, with the rapidity of respiration. The tortoise and the rabbit occupy abnormal positions; the former showing even a higher alkalinity than birds, whilst the latter has less alkalinity than the frog. C. H. B.

Formation of Lactic Acid in Muscles. By M. Werther (*Pflüger's Archiv*, **46**, 63—92).—Sarcolactic acid is the variety of lactic acid formed both during the activity of living muscle and during the rigor which accompanies the death of muscle. In cold-blooded animals, this acid passes, under certain conditions, into the urine (Marcuse, Nebelthan). During *rigor mortis*, the percentage of glycogen in the muscle diminishes, the possibility that this is due to putrefaction being excluded. This last conclusion is opposed to that of R. Böhm, who states that the glycogen remains unaltered in amount during rigor (*Pflüger's Archiv*, **23**). W. D. H.

Formation of Lactic Acid in Muscles. By R. Böhm (*Pflüger's Archiv*, **46**, 265—266).—In answer to the preceding paper, the author reaffirms his previous statements. W. D. H.

The Influence of drinking large quantities of Water on the Excretion of Uric Acid. By B. Schöndorff (*Pflüger's Archiv*, **46**, 529—551).—After a very complete summary of the literature relating to the influence of various drugs and other agents on the excretion of uric acid, the paper is more particularly concerned with the influence of taking large quantities of water on the excretion of the acid. Several investigators, especially Genth (*Unters. ü. d. Einfluss d. Wassertrinkens a. d. Stoffwechsel*, Wiesbaden, 1856), have stated that such a procedure, whilst increasing the total output of nitrogen (a statement since confirmed by many physiologists), diminishes that of uric acid. Genth, and those who agree with him on this latter point, used for the estimation of uric acid the very imperfect method of Heintz; in the present research, which was carried out on the author's own person, uric acid was estimated by the Fokker-Salkowski process. The total nitrogen was estimated by titration with mercuric nitrate. The outcome of the experiments is that whilst the total nitrogen is increased, the drinking of large quantities of water has practically no influence on the uric acid.

Observations were made daily, and the following table gives the average amounts of water taken and of uric acid excreted *per diem.*

Condition of experiment.	Total nitrogen.	Uric acid.
Ordinary diet..................	18·5 grams.	1·18 grams.
Ordinary diet + 2000 c.c. water..	20·4 „	0·93 „
Ordinary diet + 4000 c.c. water..	20·6 „	1·01 „
Ordinary diet + 1000 c.c. water..	23·1 „	1·14 „

W. D. H.

Sweat of the Horse. By F. Smith (*J. Physiol.*, **11**, 497—503).—The composition of the secretion of horse's sweat was investigated because debility follows excessive sweating in these animals. The explanation probably is that proteïds leave the system in the sweat of horses (see also Leclerc, Abstr., 1888, 1320). The excretion can be kept under control by the process of clipping horses in the winter.

500 c.c. of the secretion was collected; it was alkaline, and was found to have the following percentage composition:—

Water..........	94·3776		
Organic matter..	0·5288	Serum albumin	0·1049
		Serum globulin	0·3273
		Fat	0·0020
Ash	5·0936	Chlorine	0·3300
		Lime	0·0940
		Magnesia	0·2195
		Phosphoric acid	traces
		Sulphuric acid......	
		Soda	0·8265
		Potash	1·2135

Peptones and albumoses are absent, so also is sugar. The amount of proteïd is much increased when the horse is in "bad condition." The small amount of fat formed probably indicates that the material investigated was really sweat, and not sebum. Ether extracts from the sweat an organic, crystalline substance, which is not benzoic acid, but the exact nature of which was not definitely determined. The mineral substances are nearly ten times larger than the organic, the two most prominent metals being potassium and sodium. There would appear to be a close connection between the amount of these salts excreted by the skin and by the kidneys, for during work, when the skin is active, less potash and soda are eliminated in the urine than during rest. W. D. H.

Excretion of Nitrogen in Sweat. By P. ARGUTINSKY (*Pflüger's Archiv*, **46**, 594—600).—It is shown that there is an increase of the output of nitrogen during excessive muscular work; and that, moreover, the sweat poured out during such work contains more nitrogen than it normally does.

No reference is made to the experiments of North (Abstr., 1886, 569), of which these are merely confirmatory. W. D. H.

Influence of Muscular Work on the Output of Urea. By L. BLEIBTREU (*Pflüger's Archiv*, **46**, 601—607).—The urea in the urine obtained in one of Argutinsky's series of experiments (preceding abstract) was estimated by the method introduced by the author and E. Pflüger (Abstr., 1890, 308). Represented by curves, the output of total nitrogen and of urea are shown to be closely parallel; the increase of both is most marked during the day of the work (walking), and it was not until three days afterwards that they reached the normal level. W. D. H.

The Relation of Dextrose to the Proteïds of the Blood. By F. SCHENK (*Pflüger's Archiv*, **46**, 607—615).—If dextrose is added to blood, serum, or solutions of proteïds, and the fluid is boiled and filtered to separate the proteïds, a portion only (often less than half) of the sugar is discoverable in the filtrate and washings of the coagulum. If the clot is washed with water and with alcohol until no reducing substance passes into solution, and the clot is then boiled with dilute hydrochloric acid, a reducing substance passes into solution in quantities corresponding with the amount of sugar formerly lost. It is, therefore, probable that, during coagulation, some of the dextrose combines with the proteïds. W. D. H.

Diamines and Cystinuria. By L. v. UDRÁNSZKY and E. BAUMANN (*Zeit. physiol. Chem.*, **15**, 77—92).—In a previous communication (Abstr., 1889, 1024), it was shown that the urine and fæces of patients suffering from cystinuria contain diamines (ptomaïnes), and that their formation is the result of bacterial activity in the intestinal canal. The cystin, on the other hand, is the result of disordered metabolism. In dogs, it is possible to produce a sort of artificial cystinuria; on administering halogen substitution products of benzene to these animals, mercapturic acid (from cystin) is passed in the urine in combination with glycuronic acid; this, however, does not occur in the human subject. A possible explanation of the association of cystinuria with diaminuria is that the diamines produced in the intestine unite with cystin in the tissues (which under normal circumstances is further metabolised); and that this compound is dissociated during the act of secretion in the kidneys. In order to see whether this will hold, dogs were fed on diamines, and their urine examined. The first diamine used was ethylenediamine; 1·5 grams of this was given to a dog, but the search for it in the urine passed subsequently gave a negative result. The method employed in the isolation of diamines from the urine was that of forming benzoyl compounds of these substances (Abstr., 1888, 1296). A larger dose was then given, namely, 3·6 grams, and 0·4 gram of dibenzoylethylenediamine was separated from the urine. No trace of the base was found in the fæces. Cystin was absent from the urine, or at least there was no more lead sulphide formed on boiling the urine with sodium hydroxide and lead acetate than normally is the case.

With tetramethylenediamine (putrescine), the results were the same; with a large dose, 3 grams, a mere trace (0·05 gram) of the benzoyl compound was separated from the urine.

With pentamethylenediamine (cadaverine), the results were also practically the same. The specimen of the base used was found to consist of two isomerides; the one with the higher melting point was the least abundant, but in the small amount of the benzoyl compound separated from the urine, it was the more abundant, being seemingly less readily destroyed in the organism. Such experiments entirely negative the idea that the cause of cystinuria is the formation of diamines in the alimentary canal. The possibility, however, remains that some other unknown substance accompanying the diamines may act in this way. If this hypothesis is correct, and if this substance is produced by bacteria, anti-bacterial drugs should lessen the amount of cystin in the urine. Mester has already shown (Abstr., 1890, 189) that salol and sulphur have no such effect. In the present research, the influence of washing out the large intestine of patients suffering from cystinuria, with large quantities of water, was observed. The cystin in the urine was estimated as benzoylcystin, and its amount, and also the amount of diamines in the urine, remained practically unaltered. The estimation of oxidised and non-oxidised sulphur, by Mester's method (Abstr., 1890, 189), confirmed this conclusion.

The question of the relation of cystinuria to diaminuria is, therefore, at present unanswered. W. D. H.

Absorption of Mercury Salicylate. By L. BÖHM (*Zeit. physiol. Chem.*, **15**, 1—36).—Much of the present paper is a dissertation on the methods of detecting and estimating mercury in organic mixtures like the urine and fæces. The method adopted in the research is a modification of that of Winternitz (*Arch. exper. Path. u. Pharm.*, **25**, 225). Doses of mercury salicylate were given to a cow, but no mercury was found in the urine or milk. An experiment was then made on a dog; the urine, bile, blood, fæces, and tissues, were examined. 1·5 grams of mercury salicylate (containing 0·85 gram of mercury) was given. Of this the fæces yielded 0·4; the remainder was absorbed, and found either in the tissues or excretions. Comparing this with previous similar researches with non-poisonous doses of calomel, the conclusion is drawn that much more mercury can be absorbed into the system from the salicylate than from calomel. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Apparatus for the Manufacture of Pure Yeast. By A. FERNBACH (*Bull. Soc. Chim.* [3], **4**, 113—116).—The apparatus consists of a tinned-copper cylinder provided with a movable head, which can be adapted hermetically to the body by means of screw clamps and a caoutchouc washer; through orifices in the head, tubes pass by which steam can be passed into the vessel, as also filtered air, which makes its escape into the liquid from small orifices in a flat coil at the base of the cylinder. The clear wort is boiled in the vessel, and steam is passed through to completely sterilise it; all the orifices are then closed by tubes containing cotton-wool; on cooling, the yeast is sown, and while growing a current of filtered air is driven through the spiral, so that the fungus is grown under aërobiotic conditions. The yield obtained is very good; a wort derived from 3 kilos. of malt at 63—65° furnishing a crop of 300 grams of pressed yeast in eight days. T. G. N.

The Nitrifying Process and its Specific Ferment. By P. F. FRANKLAND and G. C. FRANKLAND (*Proc. Roy. Soc.*, **47**, 296—298).—Nitrification was induced in an ammoniacal solution by means of a small quantity of garden soil, and then carried through 24 generations. Gelatin plates were prepared from several of the generations, and the resulting colonies inoculated into ammoniacal solutions, but in no case did nitrification ensue.

Experiments were then made to isolate the nitrifying organism by dilution with sterilised distilled water. When an attenuation of 1 part of original solution in 1,000,000 had been reached in three different cases, the liquids thus produced behaved as follows: One nitrified but refused to grow in gelatin-peptone; another produced a growth but would not nitrify; whilst the third did both. It was thus shown that the organisms were reduced to two, one of which caused nitrification. Under the microscope, this appeared to be a bacillus scarcely longer than broad. Although it will not grow in gelatin when inoculated from dilute media, it produces a characteristic slow growth in broth, which nitrifies ammoniacal solutions, and also grows in gelatin. The form of the organism from the broth is slightly different from the original organism, but the identity of the two is established by the former returning to the original form when grown again in ammoniacal solution. J. W.

A Bacteria-killing Globulin. By E. H. HANKIN (*Proc. Roy. Soc.*, **48**, 93—101).—The results described in this paper were arrived at by the author while trying to discover the nature of the substance to which the bacteria-killing powers of the blood serum is due. Halliburton's cell-globulin-β was extracted from the lymphatic glands of an animal by sodium sulphate solution. It was found to have the power of killing anthrax bacilli, which property seems to distinguish it from fibrin ferment. This bacteria-killing power is of the same nature as that possessed by blood serum, which, therefore, probably acts in virtue of the same or of some allied substance. From his experiments, the author further concludes that, inasmuch as it is possible to obtain from the cells that are, or can become, phagocytes, a substance having bacteria-killing powers, it may be supposed that phagocytes can not only kill microbes that they have ingested, but also do this by breaking down, and liberating their contents.

J. W.

Antiseptic Action of Methylene Fluoride. By C. CHABRIÉ (*Compt. rend*, **111**, 748—750).—Methylene fluoride prevents the development of the pyogenic bacterium of urine and kills the bacteria already developed. It has no irritating action on the digital membrane or mesentery of a frog. C. H. B.

Acquisition of Atmospheric Nitrogen by Plants. By W. O. ATWATER and C. D. WOODS (*Amer. Chem. J.*, **12**, 526—545).—The authors describe a very large number of experiments with peas, oats, and corn, which confirm the view that nitrogen is readily absorbed from the atmosphere by these plants, when treated with "soil-infusion," and that the gain of nitrogen is dependent on the number of root-tubercles which the application of "soil-infusion" induces. (Compare Lawes and Gilbert, Abstr., 1889, 814, and *Phil. Trans.*, 1889, 1—107.) G. T. M.

Fixation of Gaseous Nitrogen by Leguminosæ. By T. SCHLOESING, JUN., and E. LAURENT (*Compt. rend.*, **111**, 750—753).—Leguminosæ were grown in closed vessels, so arranged that the gases introduced and withdrawn (air, carbonic anhydride, nitrogen, and oxygen) could be accurately measured and analysed. When the legumes had been watered with an infusion of nodosities from other plants of the same order, there was an absorption of nitrogen much greater than could be attributed to errors of experiment. Where the legumes had not been inoculated in this way, and, consequently, were free from nodosities, no such absorption of nitrogen was observed. The results obtained by direct measurement, therefore, agree with the result obtained indirectly from gravimetric analyses.

Berthelot (*ibid.*, 753) regards these results as a final proof that, under the influence of microbes, legumes can utilise and fix the gaseous nitrogen of the atmosphere. C. H. B.

The Fungus-symbiosis of the Leguminosæ. By B. FRANK (*Landw. Jahrb.*, **19**, 523—640).—A large part of the paper is devoted to the description and discussion of experiments and microscopic observations relating to the mode of acquisition of organisms by leguminous plants; the cultivation of the organisms, their relations to the plants, and the *rôle* of the infected plant, &c.

In order to ascertain the influence exerted by the organism (which he terms *Rhizobium leguminosarum*), quantitative experiments were made with beans, peans, and lupins, grown in ignited sand, in sandy soil, and in humous soil. In some experiments, the soil was sterilised, in others it was seeded with soil organisms, and to some nitrate was applied. The results of the experiments, as well as those obtained with oats and rape, are given in the following table. Three or four, or more, pots were used for each experiment; at the conclusion the soil of all the similar pots was mixed; and the produce was also united and mixed for analysis. The soils used for microbe seeding were:—Sandy soil (3 and 16), bean soil (4), pea soil (9), meadow soil (17), and lupin soil (18). 4 grams of soil was given to each pot, for the purpose of seeding. The amount of soil used for each experiment (not pot) is given at the headings of each series.

	Dry produce (grams).	Nitrogen (grams).							
		At commencement.				At conclusion.			
		Soil.	Seeding or nitrate.	Seeds.	Total.	Soil.	Produce.	Total.	Gain or loss.
Beans in Sandy Soil (12 *kilos.*).									
1	15·431	1·1622	—	0·0668	1·2290	3·7813	0·1038	3·8851	2·6561
2*	17·415	1·1622	—	0·0668	1·2290	2·6820	0·1174	2·7994	1·5704
3†	17·375	1·1622	0·0012	0·0668	1·2302	1·3410	0·1560	1·4970	0·2668
4†	11·236	1·1622	0·0228	0·0668	1·2518	2·5128	0·1203	2·6331	1·3813
Beans in Humous Soil (8·44 *kilos.*).									
5	44·488	12·820	—	0·068	12·887	14·973	0·831	15·804	2·917
6*	64·412	12·820	—	0·068	12·887	15·344	1·002	16·346	3·459
Peas in Ignited Sand.									
7	2·994	—	—	0·036	0·036	—	0·026	—	−0·010
8‡	5·392	—	0·119	0·030	0·149	—	0·072	—	−0·077
9†	12·089	—	0·004	0·024	0·028	—	0·230	—	+0·202
Peas in Sandy Loam (15·3 *kilos.*).									
10	10·136	6·750	—	0·077	6·827	6·750	0·200	6·950	0·123
11*	15·007	6·750	—	0·072	6·822	6·750	0·333	7·083	0·161
Lupins in Ignited Sand.									
12	4·061	—	—	0·028	0·028	—	0·041	—	0·013
13‡	7·202	—	0·225	0·035	0·260	—	0·094	—	−0·166
Lupins in Sandy Soil (18 *kilos.*).									
14§	14·767	1·450	—	0·035	1·485	2·371	0·361	2·732	1·247
15*	11·455	1·740	—	0·042	1·782	3·280	0·144	3·424	1·642
16†	17·925	1·740	—	0·042	1·782	2·446	0·300	2·746	0·964
17†	16·099	1·740	0·730	0·042	2·512	3·433	0·304	3·737	1·225
18†	38·754	1·740	0·006	0·042	1·788	4·404	0·777	5·181	3·393

* Sterilised. † Sterilised and seeded. ‡ Nitrate.

§ One pot less than 15—18; 15 kilos. of soil.

	Dry produce (grams).	Nitrogen (grams).							
		At commencement.				At conclusion.			
		Soil.	Seeding or nitrate.	Seeds.	Total.	Soil.	Produce.	Total.	Gain or loss.
Oats (19) *and Rape* (20) *in Heavy Loam* (8·8 *kilos.*).									
19	32·520	10·384	—	0·014	10·398	11·528	0·487	12·015	1·617
20	30·180	10·384	—	0·003	10·387	11·000	0 377	11·377	0·990
Lupins (21) *and Bare Soil* (22) (*Sandy Soil* 12 *kilos.*).									
21	8·480	1·154	—	0·070	1·224	2·172	0·184	2·356	1·131
22	—	1·154	—	—	1·154	2 062	—	2·062	0·908

With regard to beans, the growth was always only slight in poor soil, whether microbe-seeded or not; beans therefore resemble non-leguminous plants. The fungus in symbiosis with beans has the character of a parasite, and is fed by the plant without assisting it in return. Lupins assimilate a small amount of nitrogen when free from organisms, but much more when seeded. Peas are only able to fix nitrogen when microbe-seeded, or when grown in soil, or in sand containing organic matter (compare Abstr., 1890, 1020). In every case (except those of peas grown in sandy soil) there was a gain of nitrogen in the soil. The gain which takes place in bare soil (Experiment 22) is attributed to the presence of algæ under the influence of light and moisture. The results obtained with oats and rape are given in support of the author's view that the power of assimilating free nitrogen by plants is not confined to the *Leguminosæ*, but is as general as the assimilation of carbonic anhydride. The nodule-organisms could not be cultivated except in nitrogenous menstrua, and are, therefore, assumed to be incapable of assimilating nitrogen. The high percentage of nitrogen in the nodules, and the presence of starch in them, indicate that the building up of proteïds takes place in them. At the same time, it is hardly conceivable that the fixation of free nitrogen takes place in the underground organs of the plant. It might be suggested that nitric nitrogen is formed, which yields proteïds with starch; but the fact that no nitrates or nitrites could be detected (by diphenylamine) in the nodules, although nitric acid was found in the roots of peas (but not lupins), is opposed to this view. On the other hand, amides occur in all parts of the plants, and also in the nodules; and it is probable that in the first instance, the free nitrogen of the air combines with the elements of a non-nitrogenous carbon compound present in the leaves, where it is first produced, to form an amide, and that this finds its way into the nodules, where it reacts with starch and yields proteïds. The fixation therefore, takes place in the leaves.

The author considers that there is only one nodule organism, common to all leguminous plants, and that it is present in all natural soils, although in varying amounts (compare Hellriegel and Wilfarth, *Ber. deut. bot. Ges.*, **7**, 138). N. H. J. M.

NOTE.—Prażmowski's experiments with pure cultivations of nodule-organisms from peas indicate that the organisms have the power of assimilating free nitrogen, in absence of any other source, although the amount of nitrogen assimilated by the organisms apart from the plant is only small. In view of the great change which the organisms undergo in symbiosis with plants, the difference is not remarkable (*Landw. Versuchs-Stat.*, **38**, 55). N. H. J. M.

Nature of Reserve Cellulose and its Mode of Solution during Germination of Seed. By REISS (*Ann. Agron.*, **16**, 478—480).—The cellulose forming the thickened walls of the albumen (botanical) containing cells of many seeds dissolves during germination, and assists in the nutrition of the young seedling; it is, therefore, called reserve cellulose. In date seeds, it is the portion of the cell-wall nearest the cell-centre which dissolves; in asparagus seeds, the middle layer between neighbouring cells and the inner layer next the protoplasm both dissolve; garlic seeds are similar, but the thickened walls have innumerable fine branching canals, which the author calls canals of corrosion, and which facilitate the solution. Even in seeds whose cell-walls are not thickened, the cellulose dissolves, commencing at the middle layers and proceeding towards the internal linings. In other seeds (balsam, monkshood, cyclamen, for example), this reserve cellulose is replaced by an amyloïd substance, which also is traversed by canals of corrosion and dissolves. It is more soluble in 50 per cent. nitric acid than reserve cellulose. Reserve cellulose cannot be separated by Hofmeister's process for "crude fibre," since a portion dissolves in ammonia. The product of its hydrolysis (studied in the "albumen" of *Phytelephas*) with sulphuric acid is *seminin*, a lævogyratory substance or mixture; the dextrins of ordinary cellulose formed in the same way being dextrogyratory. Submitted to further hydrolytic treatment, seminin gives a new sugar, fermentable, reducing, and dextogyratory, which the author calls *seminose.*

Seminose gives with phenylhydrazine acetate, in the cold, a colourless hydrazone sparingly soluble in water; it gives also an isonitroso-compound in fine, colourless crystals, analogous to the compound Rischbieth obtained with galactose, but not with dextrose, lævulose, or arabinose. Seminose is precipitated by lead acetate in neutral aqueous solution, and this, according to the author, distinguishes it from Fischer and Hirschberger's *mannose*, the only other known sugar giving a slightly soluble phenylhydrazone; mannose is precipitable only by ammoniacal lead acetate. The abstractor to the *Ann. Agron.*, however, points out that Fischer and Hirschberger have recently found that mannose is rapidly precipitated from strong solutions by lead acetate, and that these authors consider seminose to be identical with mannose. Seminin exists ready formed in the seed of *Phytelephas*; it has been obtained by saccharifying the reserve cellulose of seeds of date, *Chamærops*, *Lodoïcea*, *Elais guineensis*, *Allium cepa*, asparagus, *Iris pseudoacorus*, fennel, coffee, and nux vomica. The *seedlings* contain only ordinary cellulose, the reserve cellulose having been perhaps transformed into seminose during germination. Seminose, however, was not discovered in germinating date seeds, but plenty of (probably) dextrose. Hydrolysis of the amyloïd substance of balsam, monkshood, primrose, and peony seeds gave dextrose, not seminose. J. M. H. M.

Conversion Products of Starch. By A. MARCACCI (*Bied. Centr.*, **19**, 792; from *Staz. sper. agr. ital.*, **18**, 618—619).—Potato starch, even in quite ripe potatoes, becomes converted into cane-sugar; and barley and wheat grains, in germinating, double the amount of cane-sugar at the expense of the starch they originally contained. Samples of potato meal and finely-cut potatoes were dried, some in the sun, and some in a drying oven at 45°; an increase of cane-sugar was observed in the artificially dried potato; in the cut potatoes, the amount of sugar was more than doubled when dried at 45°. In germination, potatoes gain saccharose; the starch is probably converted, first into saccharose, and then into glucose. The formation of dextrin is not necessary.

Starch is formed by the elimination of water. Unripe wheat grains contain much glucose and saccharose; when the same amount of grains were examined after being dried in the sun, the sugar had disappeared, and was found to be replaced by starch.

N. H. J. M.

The Presence of Cholesterol and a Soluble Carbohydrate in Melon Seeds. By C. FORTI (*Chem. Centr.*, 1890, ii, 581—582; from *Staz. sperim. agric. ital.*, **18**, 580—588).—Determinations of the amount of phosphorus in the ether extract of the seeds of melons showed it to be present in the proportion of 0·0189 to 0·02 per cent. It exists as lecithin, and is equivalent to 0·494 to 0·526 per cent. of the latter. Adopting the views of Schulze and Steiger (Abstr., 1889, 645), that the substance should be extracted with alcohol in order to obtain all the lecithin, the author found 0·024 per cent. of phosphorus, equivalent to 0·629 per cent. of lecithin. The seeds contain about 49 per cent. of oil, which is almost free from free fatty acids; the distillate of 25 grams neutralised 3·2 c.c. of decinormal barium hydroxide solution.

Having saponified the fat with sodium hydroxide, the dry soap was treated with ether, which extracted a substance, soluble in alcohol; this crystallised in yellowish, fatty scales, and did not consist entirely of fat and wax. When treated with alcoholic potash, a non-saponifiable residue was left, which proved to be cholesterol. It melted at 160°, contained 1 mol. of water of crystallisation, and has the formula $C_{26}H_{44}O,H_2O$; the water separates at 100°. A minute portion of this cholesterol, when treated with a drop of nitric acid and evaporated to dryness, left a yellow residue, which became coloured bright red by ammonia; the coloration was intensified by the addition of sodium hydroxide. The chloroform solution was coloured brown by sulphuric acid, the coloration changing to violet and finally yellow after a time, whilst the sulphuric acid layer became reddish-brown and fluoresced. The chloroform solution, when shaken with a little ferric chloride and hydrochloric acid and evaporated to dryness, left a yellow residue, which, when again treated with chloroform in the cold and then gently warmed, became violet, and left a dirty-green residue on evaporating to dryness. The specific rotatory power of the substance in chloroform solution was $[\alpha]_D = 14{\cdot}17$.

The *acetyl derivative*, $C_{26}H_{45}{\cdot}OAc$, crystallised from absolute alcohol in lustrous plates melting at 170—173° to a lemon yellow fluid. When boiled with potash, potassium acetate and the original cholesterol are obtained. The acetyl derivative of cholesterol from bile crystallises in needles and melts at 111°. The *benzoyl derivative* is very slightly soluble in alcohol, and separates from the solution, on cooling, in small crystals which melt at 172—174°. These properties of this cholesterin differ from those of the better-known cholesterol, and require further investigation.

The soluble carbohydrate of melon seeds is dextro-rotatory, even after treatment with acids, and appears to belong to the galactan group. It forms an amorphous, yellowish-white, very hygroscopic powder. After boiling with hydrochloric acid, the phenylhydrazine derivative of the product was prepared; this melts at 184—186°.

J. W. L.

Amount of Theïne in Tea. By B. H. Paul and A. J. Cownley (*Pharm. J. Trans.*, [3], **21**, 61).—Believing that the amount of theïne in tea has commonly been understated, owing to defective methods of determination, the authors have made a further series of analyses. Eight samples, purchased at grocers' shops in the ordinary way, yielded from 2·93 to 3·93, average 3·39, per cent. of theïne calculated on the dried tea. Four samples of China tea gave 2·42, 3·50, 3·63, and 3·78 per cent. respectively. Four samples of cheap Japan Congou averaged 2·80 per cent. theïne, but as much as 4·10 per cent. was found in a Java tea. Japan and China teas appear, therefore, generally inferior as regards content of theïne to Indian or Ceylon teas, which, on the other hand, are approached by Java tea. In these analyses duplicate determinations of the theïne were made with magnesia and with lime —the only methods that are trustworthy. R. R.

Acidity of Potato Starch. By Saare (*Ann. Agron.*, **16**, 471).—Most samples of potato starch are slightly acid, and the acid is said to increase with age, but the author believes that perfectly neutral starch can be obtained, and that it will, if properly dried, keep without developing the slightest acidity. Discussing the source of the acid, the author remarks that potato-juice is naturally acid, and that the starch, if imperfectly washed, will retain some of this; that lactic and butyric acids may be developed by bacterial fermentations during manufacture; and that sulphuric and sulphurous acids are sometimes used in the process of manufacture. The acid, whatever it is, cannot be perfectly removed by washing with pure water, but if hard water be used, the acid becomes neutralised by the lime. J. M. H. M.

Maize dried in the Field and as Silage. By H. P. ARMSBY and W. H. CALDWELL (*Bied. Centr.*, **19**, 753—756; from *Agric. Science*, **4**, 119—146).—A maize field, manured with farm-yard manure, Carolina phosphate, and blood meal, was divided into three parts, the produce of two divisions put into two silos, and that of the third division kept for a month on the field to dry. The one silo was filled quickly (one day) and contained 17,000 kilos.; the second was filled slowly (seven days), and contained about 15,600 kilos. The weight of the hay was 4300 kilos.

The maize put into the silos had the following composition; (1) refers to the quickly and (2) to the slowly filled silo :—

	Water.	Ash.	Proteïd.	Non-proteïd.	Crude fibre.	Non-nitrogenous extract.	Fat.
1.	76·90	1·97	1·63	0·15	5·16	13·42	0·77
2.	76·26	1·43	1·44	0·30	5·65	14·26	0·66

The temperature rose quickly at first, especially at the surface, and more in the slowly-filled silo than in the other one. The following table shows the total amount of produce (in kilos.) in the two silos (1 and 2, as before) and of hay (3) :—

	Dry substance.	Ash.	Proteïd.	Non-proteïd.	Crude fibre.	Non-nitrogenous extract.	Fat.
1.	3920	333	277	27	876	2276	131
2.	3713	238	228	48	832	2284	104
3.	2677	195	176	26	617	1579	82

Experiments were made with two Devonshire bullocks to determine the digestibility of the different preparations, the food being given for seven days before the experiments began. Samples of food and fæces were taken daily for analysis, and the animals were weighed each day before and after drinking. The amounts given were: silage, (1) 20·412 kilos., (2) 15·889 kilos. of fresh, or 5·655 and 4·662 kilos. of dry substance; hay, 7 265 or 5·263 kilos. of dry matter. The results show that the dry substance of the maize hay is the most readily digested, and that that of the silage from the slowly filled silo is the least digestible. The digestibility of the proteïd is nearly the same in each case, whilst the fat of the hay seems to be less digestible than that of the ensilage. The variation in the digestibility of the dry substance is chiefly due to differences in the digestibility of the crude fibre and the non-nitrogenous extract. The results are given in tables, together with those of Woll and of Sturtevant. The results do not indicate any great difference of digestibility between maize ensilage and maize hay.

The ensilage lost (in the silo) half as much dry matter and two-fifths as much proteïd as the hay lost; but a quarter of the proteïd was converted into non-proteïd. The hay lost 14 per cent. of crude fibre; no such loss was observed in the case of the ensilage.

N. H. J. M.

Wine Analyses. By E. BOSSHARD (*Zeit. anal. Chem.*, 1890, 551—556).—The results are given of the analysis, by the usual methods, of 24 specimens of wine from the Valtellina, 24 from the Coire Valley, 5 specimens of Medoc (1883—1887), and 4 Tuscan wines. The composition of the Valtellina wines does not differ notably from that of other red wines, the alcohol ranging from 7·83 (in a cheap specimen of Veltliner) to 14·43 vols. per cent. (in a fine Valgella), with an average of 10·97, and the solid residue from 17·24 to 26·45 (average 23·0) grams per litre. The ash of several of the varieties contained much manganese.

The wines of the Coire Valley are, on the average, less alcoholic (max. 11·44, min. 8·01; average 9·73), but contain rather more extractive matter (max. 25·61, min. 19·86; average 24·05). In composition they show considerable resemblance to Burgundy, and, if more carefully fermented, they would take a much higher position than they do at present. M. J. S.

Analytical Chemistry.

Iodometric Estimation of Acids and Alkalis. By M. Gröger (*Zeit. ang. Chem.*, 1890, 353—356).—The author has made a careful study of the conditions under which acidimetry and alkalimetry can be performed by means of the reaction $KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + I_6$. A neutral mixture of iodide and iodate cannot be made by dissolving iodine in potash, but must be prepared by mixing, in the proper proportions, neutral solutions of the respective salts shortly before use. On adding an excess of such a mixture to a mineral acid, and titrating the liberated iodine by thiosulphate, the result agrees exactly with that of a direct titration by an alkali. The hydroxides of potassium, sodium, and ammonium can all be estimated by adding an excess of standard acid and titrating the excess as above. Alkaline carbonates can be approximately titrated in the cold by a similar procedure, if the first disappearance of the iodine is taken as the end point; but the carbonic acid in solution slowly liberates a further quantity of iodine, so that to obtain exact results it is advisable to boil out the carbonic anhydride and cool before adding the iodine salts. The same applies to alkaline sulphides. This method may be used in many cases for dark-coloured liquids in which the change of litmus or methyl orange could not be seen. It cannot be employed for organic acids, unless the iodine be distilled out. The author is investigating this point. M. J. S.

Detection of Minute Quantities of Hydrogen Peroxide and of Uranium. By T. Fairley (*Chem. News*, **62**, 227).—0·24 milligram of hydrogen peroxide may be detected by adding 1 or 2 c.c of ether to 5 c.c. of the peroxide solution, and a small drop of a 10 per cent. chromic acid solution, and even 0·10 milligram can be detected by using 1 c.c. of peroxide solution and 1 c.c. of ether; but by the use of 5 c.c. of a dilute uranium nitrate solution 0·05 to 0·025 milligram of hydrogen peroxide in 5 c.c. can be rendered evident; moreover, as little as 0·5 to 0·25 milligram of uranium can be detected and very small quantities determined by this method of treatment.

D. A. L.

Direct Estimation of Bromine in Mixtures of Alkaline Bromides and Iodides. By F. A. Gooch and J. R. Ensign (*Amer. J. Sci.* [3], **40**, 145—152).—In a former paper (Abstr., 1890, 920), two methods were described for the direct estimation of chlorine in mixtures of alkaline chlorides and iodides, based on the action of oxidising agents, in the presence of free sulphuric acid, on dilute solutions of the haloïd salts at the boiling temperature. A study of the behaviour of mixtures of alkaline bromides and iodides, when treated in a similar manner, leads to the conclusion that only one of the above two methods is applicable to the separation of bromine from iodine, and then only under modified conditions. With the necessary modifications, however, it is good, and may be applied in the following manner:—The neutral solution containing the bromide or iodide is diluted to 600 or 700 c.c., and 1 to 1·5 c.c. of concentrated sulphuric acid, or better, 2 to 3 c.c. of the mixture made by diluting the acid with an equal volume of water, is added, a sufficient amount of pure sodium or potassium nitrite is introduced (or, if it is preferred, the gas generated by the action of dilute sulphuric acid on the ordinary nitrite, and introduced from the outside, may be employed instead) and the liquid is boiled, after trapping the flask as formerly described, until the colour has vanished and the escaping steam no longer gives to litmus the colour characteristic of iodine (see next abstract). The residual liquid is treated with an excess of silver nitrate, and the precipitated bromide collected, dried, and weighed. The process of boiling need not extend beyond half an hour, or a little more, and care should be taken that the volume of the liquid shall never be less than 500 c.c. The solution should not contain more than about 0·5 gram each of the bromide and iodide. The presence of 0·5 gram of potassium chloride does not affect the sharpness of the separation. H. C.

Rapid Method for the Detection of Iodine, Bromine, and Chlorine in presence of one another. By F. A. Gooch and F. T. Brooks (*Amer. J. Sci.* [3], **40**, 283—290).—The solution of the substance under examination is acidified with dilute sulphuric acid, and treated with a drop or two of a solution of sodium or potassium nitrite free from chlorine. Unless the amount present is small, the iodine shows itself in the colour of the solution and in the vapours which escape. Small amounts may be detected by shaking with carbon bisulphide, or by heating the solution and testing the escaping fumes with red litmus paper, which is coloured greyish-blue by iodine. The whole of the iodine must be removed previous to making the tests for bromine and chlorine; and this is done by adding a sufficient amount of nitrite and sulphuric acid to liberate the iodine, and heating the liquid until the vapour has no effect on red litmus paper. A portion of the solution is then tested for bromine by cautiously adding a dilute solution of sodium hypochlorite and shaking with colourless carbon bisulphide. Another portion of the solution is evaporated to dryness, and treated with potassium dichromate and sulphuric acid; the fumes of chromyl chloride which are given off on warming are condensed and converted into chromic acid, and the latter detected by means of lead acetate. H. C.

Priestley's Method of Measuring Oxygen in Air. By J. A. WANKLYN (*Chem. News*, **62**, 263).—Priestley's method for measuring oxygen in the air by observing the diminution of volume on the addition of a measured volume of nitric oxide has been condemned as inaccurate; the author of the present note states that the inaccuracy was due to the oxygen present in the water through which the nitric oxide bubbled. This source of inaccuracy can be avoided, when using a Hempel apparatus, by measuring the air in the gas burette, and then passing it into an absorption pipette containing water. The nitric oxide is introduced into the gas burette and measured, and then (without bubbling through water) passed to the air in the absorption pipette; after the nitric peroxide formed has been absorbed by the water in the absorption pipette, the gas is passed back into the gas pipette and again measured.

D. A. L.

Estimation of Sulphur in Copper. By H. J. PHILLIPS (*Chem. News*, **62**, 239—240).—Dissolve 10 grams of the sample in nitric acid of sp. gr. 1·430, evaporate to dryness, redissolve in dilute nitric acid, examine any residue for sulphur, dilute the filtrate to 800 c.c., heat to 70°, add a small quantity of hydrochloric acid, and, after 12 hours, remove and estimate any silver chloride. The filtrate is evaporated considerably, 50 c.c. of hydrochloric acid of sp. gr. 1·16 added, and the evaporation continued to dryness; the residue is dissolved in a minimum quantity of water, again treated with hydrochloric acid, and evaporated. It is now dissolved in 300 c.c. of hydrochloric acid, diluted to 700 c.c., heated to boiling, barium chloride stirred in, and, after 24 hours, the precipitate collected and treated as usual. Lead sulphate, being soluble in copper nitrate solution, frequently passes completely into solution, and has to be determined in the manner suggested. D. A. L.

The Kjeldahl-Wilfarth Method. By P. ARGUTINSKY (*Pflüger's Archiv*, **46**, 581—593).—In a large number of experiments, the Kjeldahl method of estimating nitrogen was employed, and found most satisfactory; the actual manipulations demand care, and the following points are especially insisted on:—The advisability of adding mercury to hasten the oxidation; the fact that the addition of potassium permanganate is not necessary; the collection of the distillate in a U-shaped Peligot's flask; the continuation of the distillation for 45 minutes, and the use of cochineal as indicator.

The substances investigated were urine, sweat, and fæces.

W. D. H.

Cinchonamine as a Test for Nitrates. By ARNAUD (*Ann. Chim. Phys.*, [6], **19**, 93—131).—By far the greater part of the subject-matter of this paper has been previously published by the author (Abstr., 1882, 229 and 1884, 87) and by Hesse (Abstr., 1885, 64).

The qualitative test for nitrates in plants described by the author and Padé (Abstr., 1884, 1074) can also be employed for estimating nitrates in natural waters, in the following manner:—The water is neutralised with soda or sulphuric acid, as the case may be, the chlorine in solution precipitated with silver acetate, and the slight excess of silver employed precipitated with sodium phosphate; the solution is then evaporated almost to dryness, filtered if necessary, rendered very slightly acid with a drop of dilute acetic acid, and the boiling solution mixed with a warm solution of cinchonamine sulphate. Cinchonamine nitrate is at once precipitated in a crystalline condition, and, after keeping for 12 hours in a cool place, it is separated by filtration, washed first with a cold, saturated aqueous solution of cinchonamine sulphate and then with a very small quantity of cold water, and dried at 100°. The same method can be employed with slight modifications for estimating the nitrates in plants. For this purpose, the triturated plant is extracted with boiling water; the solution evaporated to a syrup, and the residue extracted with 40 per cent. alcohol; after evaporating the alcohol, the chlorine in the solution is eliminated by means of normal lead acetate, the excess of lead removed with a few drops of sodium sulphate, and the nitric acid then precipitated with cinchonamine sulphate as described above.
F. S. K.

Phosphorus in Pig-iron, Steel, and Iron Ore. By C. JONES (*Chem. News*, **62**, 220—222, 231—232).—Various authorities are quoted and numerical analytical data furnished in proof of the efficiency of oxidation with permanganate; of washing the molybdate precipitate with sulphuric acid and ammonium sulphate instead of nitric acid and ammonium nitrate; of the use of ferrous sulphate instead of an organic acid to dissolve the precipitated manganic hydroxide, and of the employment of the author's reducing agent (filtering through powdered zinc with strong suction; Abstr., 1889, 1248) in place of adding zinc directly in the estimation of phosphorus in pig-iron, &c. The following modification of Drown's method (Abstr., 1889, 1245) is then recommended. For pig-iron and steel, dissolve in nitric acid of sp. gr. 1·135, boil for one minute, oxidise with potassium permanganate, dissolve the manganese hydroxide precipitate by adding a few fragments of ferrous sulphate free from phosphate, filter, add ammonia of sp. gr. 0·90, test the cleared solution with permanganate to be sure that the oxidation is perfect, heat to 85°, add prepared ammonium molybdate (Drown's formula), agitate for 5 minutes, filter, wash with ammonium sulphate, dissolve the phosphomolybdate in ammonia of sp. gr. 0·96, wash with water, filter, acidify with sulphuric acid, pass through the zinc powder, and titrate as usual. The correction for the zinc is ascertained by blank tests. Numerous results are given showing the efficiency of the method. Iron ores, after being treated in the usual manner, can be examined by this method; titanium and arsenic interfere with the working of the method, but in the absence of these elements an estimation of phosphorus in iron or steel can be executed in less than an hour; iron ore estimations take a little longer time.
D. A. L.

Distinction between Arsenic and Antimony. By G. Denigès (*Compt. rend.*, **111**, 824—825).—The stain obtained in Marsh's test is placed in a porcelain capsule and heated with a few drops of pure nitric acid, and a small quantity of a solution of ammonium molybdate in nitric acid is added. Antimony gives no precipitate, but if arsenic is present, arsenomolybdic acid separates as a yellow precipitate which under the microscope is seen to consist of stellate crystals with triangular arms, generally six, arranged in rectangular planes along the axes of a cube. They act on polarised light. The author believes this to be the most sensitive and characteristic test for arsenic.

To prepare the ammonium molybdate solution, 10 grams of this salt and 25 grams of ammonium nitrate are dissolved in 100 c.c. of warm water. The solution is allowed to cool, and 100 c.c. of pure nitric acid of sp. gr. 1·20 is added drop by drop with vigorous agitation. The liquid is heated on a water-bath for 10 minutes, allowed to cool, and filtered after 48 hours. C. H. B.

Sodium Carbonate: Dectection of Traces of Alkaline Hydroxides. By R. Kissling (*Zeit. ang. Chem.*, 1890, 262—263).—The author believes that his earlier experiments (*Zeit. ang. Chem.*, 1889, 323), from which he concluded that sodium carbonate gave off considerable proportions of carbonic anhydride at 400°, were vitiated by the presence of an impurity. He has repeated his experiments with several of the purest specimens of sodium carbonate and sodium hydrogen carbonate to be found in commerce. After drying at 150°, during which the sodium hydrogen carbonates lost from 36·82 to 36·84 per cent., 100 parts, heated until fritted, lost in different cases quantities which ranged from 0·03 to 0·27 parts, and, when fully fused, 0·71 to 1·05 parts. Both after fritting and after fusion sodium oxide could be detected, although after simple drying at 150° no evidence of hydroxide could be obtained. The conclusion is that ignited sodium carbonate cannot safely be employed for standardising an acid.

Dobbin's reagent for the detection of traces of alkaline hydroxides is prepared as follows:—A solution of about 5 grams of potassium iodide is mixed with sufficient mercuric chloride to just give a permanent precipitate. This is filtered off, 1 gram of ammonium chloride is added, and then dilute sodium hydroxide until a permanent precipitate is again obtained. The filtered liquid is made up to a litre. The smallest trace of an alkaline hydroxide produces a yellow colour with this reagent. M. J. S.

Analysis of the Barium Group. By C. Lüdeking (*Zeit. anal. Chem.*, **29**, 556—561).—The sensitiveness of calcium sulphate as a test for barium (cold) and strontium (hot) is not sufficient to render it a satisfactory reagent, and the presence of large proportions of calcium chloride impairs its sensitiveness to an extraordinary degree. Similarly, a solution of strontium chloride hinders the precipitation of barium by calcium sulphate to such an extent that notable proportions of barium might be entirely overlooked in a solution containing much strontium. On the other hand, very strong solutions of strontium chloride give a precipitate so instantaneously on addition of calcium sulphate that the presence of barium would certainly be inferred. Potassium chromate is free from these objections. It is a more delicate test than calcium sulphate for barium when occurring alone, and it is in no way affected by the presence of strontium or calcium. The ammonium carbonate precipitate should be dissolved in acetic acid, a saturated solution of potassium chromate added, and the mixture boiled. If 0·1 per cent of barium chloride is present, a precipitate will be produced. The strontium and calcium should be again thrown down from the filtrate by ammonium carbonate, the well washed precipitate dissolved in hydrochloric acid and tested for strontium by the spectroscope. The blue line is the best for observation. An excess of sulphuric acid is then added, the mixture boiled, filtered from strontium sulphate, and the filtrate tested for calcium.

M. J. S.

Metallurgical Assay of Lead Waste. By W. Stahl (*Zeit. anal. Chem.*, **29**, 630; from *Berg. Hutt. Zeit.*, **48**, 237).—From 5 to 10 grams of the substance is intimately mixed with 1 or 2 grams of spongy silver, reduced from the chloride by zinc, and 3 parts of a flux consisting of 1 part of soda, 1 part of potash, and 20—30 per cent. of flour, together with enough borax to dissolve the earths which may be present. The mixture is placed in a crucible, heated gently as long as combustible gases are evolved, and then more strongly for 45—60 minutes. From the weight of the button, that of the silver taken is to be deducted, and the remainder is the lead present in the waste. M. J. S.

Analysis of Sodium Aluminate. By G. Lunge (*Zeit. ang. Chem.*, 1890, 227).—A weighed quantity is dissolved, during which operation the insoluble matter may be filtered off for estimation, and an aliquot part of the solution, mixed with a drop of phenolphthaleïn, is titrated with hydrochloric acid until the pink colour disappears. The quantity used indicates the amount of soda in combination with alumina and silica. To the same portion, is now added a drop of methyl-orange, and titration with the same acid is continued until the pink colour remains permanent for five minutes. The change of colour at this stage is sluggish. This gives the amount of the alumina, since methyl-orange does not indicate the presence of acid until all the alumina is converted into chloride. The method can only be used in cases where the silicate present is small enough to be neglected. M. J. S.

Volumetric Estimation of Alumina. By G. Lunge (*Zeit. ang. Chem.*, 1890, 293—300).—A similar process to that of the author (see preceding abstract) had already been proposed by Cross and Bevan, who, however, used litmus instead of phenolphthaleïn. The original proposal to estimate alumina by titration is, however, due to Bayer (Abstr., 1886, 281, 651). Cross and Bevan found that free acid appeared in the mixture when the ratio $5SO_3 : 2Al_2O_3$ was passed. The author shows that this was most likely due to their working at too low a temperature, since towards the end of the process the alumina dissolves in the highly dilute acid with such extreme slowness, that several hours must be allowed to elapse before it can be with certainty decided that the acid is in excess. The acid consumed corresponds ultimately with the ratio $3SO_3 : Al_2O_3$, and with a moderately warm liquid (30—37°), the solution of the alumina proceeds rapidly enough to make the process a practical one. The titration with phenolphthaleïn is best performed at a boiling heat, and that with methyl-orange should be completed at about the above temperature. M. J. S.

Rapid Estimation of Manganese in Slags, Ores, &c. By F. G. MYHLERTZ (*Chem. Centr.*, 1890, ii, 607—608; *Journ. anal. Chem.*, **4**, 267).—0·5 gram of the finely pulverised mineral is mixed with 5 grams of a mixture of sodium carbonate (3 parts) and potassium nitrate (1 part) and fused carefully. After allowing it to cool, the melt is digested in hot water, and the manganate reduced by addition of 3 c.c. of alcohol, without, however, filtering. The insoluble portion containing the manganese as dioxide is then collected and washed with hot water. The filter with the insoluble part is returned to the dish, and 100 c.c. of ferrous sulphate of known strength added, stirred until all is dissolved, and the excess of ferrous sulphate determined with potassium dichromate. From the amount of ferrous sulphate oxidised by the manganese dioxide, the amount of the latter may be calculated. The estimation occupies from two to three hours.

J. W. L.

Estimation of Chromium in Chrome Iron. By L. P. KENNICUT and G. W. PATTERSON (*Zeit. anal. Chem.*, **29**, 596).—A very refractory Pennsylvanian ore was satisfactorily attacked by the following method:—About 0·3 gram of the fine powder is mixed in a platinum crucible with about 10 parts of dry sodium carbonate and 10 parts of barium peroxide, and heated over a Bunsen burner for half an hour. The mass is then treated with hydrochloric acid until a clear solution is obtained; potash is added to strongly alkaline reaction, then 5 or 6 c.c. of a 5 per cent. solution of hydrogen peroxide to re-oxidise any traces of chromic oxide, and lastly the liquid is boiled for twenty minutes to remove excess of the peroxide. After acidifying with hydrochloric acid, the chromic acid is titrated in the usual way.

M. J. S.

Separation of Tin and Antimony. By H. N. WARREN (*Chem. News*, **62**, 216).—The pulverised material, after fusion in a nickel crucible with sodium carbonate and borax, is dissolved in hydrochloric acid, and an aliquot part of the solution precipitated with hydrogen sulphide. This precipitate is collected on a plug of cotton, boiled with sodium hydroxide, and the solution of sodium sulphostannate and sulphantimonate obtained is divided into two portions: in the one, only the antimony sulphide is precipitated by boiling with excess of oxalic acid, whilst in the other, the tin and antimony sulphides are precipitated together by warming with dilute hydrochloric acid, but in both cases, the sulphides are decomposed by ignition and weighed as oxides, from which data the relative proportions are easily obtained.

D. A. L.

Estimation of Cyanogen in Coal Gas. By W. Leybold (*Chem. Centr.*, 1890, ii, 531; from *Journ. Gasbeleucht. Wasserversorg*, **33**, 383—384, 427—428).—In each of three Woulff's bottles, 20 c.c. of aqueous soda (1 : 3) is placed, to which is added a quantity of suspended ferrous hydroxide, prepared by adding 20 c.c. of soda (1 : 3) to 30 c.c. of ferrous sulphate (1 : 10), the first Woulff's bottle receiving 25 c.c., the second 15 c.c., and the third 10 c.c. of the mixture. 100 litres of the gas under examination is passed through the bottles during 1 to 1½ hours, after which the contents of the three bottles are transferred to one flask and boiled for a quarter of an hour. After settling and allowing to cool, the supernatant fluid is decanted into a 500 c.c. flask, and the insoluble ferrous hydroxide washed until free from cyanide, the filtrate being then diluted to the mark. According to whether the gas under examination has passed the first purifier or not, 100 c.c. or 200 c.c. of the solution is acidified with hydrochloric acid, excess of ferric chloride added, and the precipitated Prussian blue collected and washed with small quantities of water until free from ferric chloride. The filter, with the precipitate, is transferred to a beaker, dissolved in soda, and the solution filtered. The filtrate is evaporated in a platinum dish to 30 c.c., a considerable excess of dilute (1 : 10) sulphuric acid added, and the liquid evaporated to dryness, and ignited. The residue is dissolved in 100 c.c. of dilute (1 : 10) sulphuric acid, washed into a 250 c.c. flask with a little water, the volume being now about 150 c.c., 1 c.c. of copper sulphate solution (1 : 10) and 10 grams of pure zinc added, and the ferric oxide reduced and determined with potassium permanganate solution. J. W. L.

Estimation of Ferrocyanides in Gas Refuse. By R. Zaloziecki (*Zeit. ang. Chem.*, 1890, 301—302; see this vol., p. 247).—20 grams of the waste product is heated for a quarter of an hour on the water-bath with about 20 c.c. of 10 per cent. potash solution, then cooled, made up to 100 c.c., and filtered. As the solid residue occupies 10 c.c., 45 c.c. of the filtrate is taken and boiled until all the ammonia is driven off. A clearer solution can be obtained if the original extraction is made with lime (Leschhorn, *Zeit. ang. Chem.*, 1888, 616), and the calcium then removed from the solution by potassium carbonate. A drop of phenolphthaleïn is now added, and then acid to exact neutrality. The separation of sulphur at this stage does not prejudice the later operations. In consequence of the presence of the chlorides or sulphates formed during the neutralising, some normal alkaline carbonate (20 c.c.) must now be added, together with 5 grams of moist zinc carbonate, and the mixture heated whilst carbonic anhydride is passed through it for half an hour. It is then cooled, made up, and one-half of the clear filtrate titrated with N/10 acid, using methyl-orange as indicator. The volume of acid corresponding with the normal alkali added is subtracted, and the remainder gives the alkaline carbonate produced by the reaction. The amount of potassium carbonate found, multiplied by 46, gives the percentage of $K_4FeC_6N_6 + 3H_2O$. M. J. S.

Analysis of Wort and Beer. By H. Elion (*Zeit. ang. Chem.*, 1890, 291—298, 321—326).—For the estimation of the solid residue, the author prefers to dry at 96—97° in a stream of air of low tension. The liquids are evaporated and the residues dried in small stoppered glass vessels, 40 mm. diameter and 35 mm. high, which are placed in a cylindrical oven with a steam-jacket and exhausting pump, a regulated stream of dry air being admitted so as to maintain a pressure of only 35—45 mm. of mercury. Complete desiccation is obtained in 10—15 hours, and so little decomposition of the residue takes place that it may safely be neglected. The percentage of residue from a wort of given gravity is much smaller when estimated in this way than was found by Schultze, who dried his residues at 70—75° under atmospheric pressure, and this is shown to be only partially due to the dehydration of the maltose at the higher temperature. A complete table is given, showing the correspondence between specific gravity and percentage of extractive matters, from 1·0001 to 1·0992.

The ordinary method of estimating maltose by means of the reduction of Fehling's solution gives results which do not agree with those of practical brewing. The method employed by the author is as follows:—A flask, with a Pasteur's tube, is half filled with sterilised wort and inoculated with a trace of a pure culture of *Saccharomyces cerevisiæ*. It is then kept for several days at 25°. The yeast grows, and in about two days the wort is in full fermentation, which gradually decreases and finally stops completely. The power of reducing copper solution is now found to have greatly diminished, but not disappeared. It is shown that the amount of the diminution, if calculated as maltose, agrees almost exactly with the diminution in the amount of solid residue, and that on estimating the dextrose produced by the action of hydrochloric acid, and calculating into maltose the difference between that found in the original and that in the fermented wort, this amount agrees closely with that found by the other methods. The sugar destroyed by the fermentation is, therefore, practically all maltose, and it is shown that no maltose remains unfermented. Of these three methods, that depending on the loss of solid residue is the most free from sources of error. The essential features of the process are the use of a pure culture, and of only traces of it. The maltose is found to constitute only 86—92 per cent. of the total copper-reducing constituents of the wort.

The same process can be applied to beer. It is best to work with the sterilised beer itself, since, if the alcohol is first distilled off, a small part of the unfermentable matters is converted into sugar. When making estimations of copper reduction by the method of collecting the cuprous oxide and weighing, it is advisable to oxidise by ignition in order to get rid of some co-precipitated organic matter, but a constant weight of cupric oxide cannot be obtained. It should, therefore, be again reduced and weighed as metallic copper, when the results are perfectly constant. From numerous experiments, it is found that the largest yield of dextrose is obtained by using a solution containing about 1·5 per cent. of solid residue with $\frac{1}{20}$ of its volume of hydrochloric acid of 1·19 sp. gr., and heating for three hours in the water-bath.

The value for practical brewing of a correct knowledge of the amount of maltose in wort and beer is pointed out. It especially becomes evident that for a beer to keep well it must contain a low proportion of maltose. As long as the total copper-reducing power of the extractive matters in beer was the only guide to the amount of maltose present, this fact was obscured by the preponderance of the non-fermentable reducing substances. M. J. S.

Volumetric Estimation of Glycerol in Wine. By V. OLIVIERI and M. SPICA (*Chem. Centr.*, 1890, ii, 611—612; from *Staz. sperim. agric. ital.*, **19**, 34—41).—10 to 15 c.c. of the wine is warmed on the water-bath until all the alcohol is evaporated, the volume being maintained by addition of water. Lead acetate is then added, the precipitate filtered off, the excess of lead precipitated from the filtrate with sodium carbonate, and the filtrate concentrated on the water-bath to 15 to 20 c.c. This is distilled under diminished pressure, by which means the glycerol passes over below 200°. After all has distilled, the retort is rinsed down with 5 c.c. of water, and the distillation repeated. The mixed distillates are acidified with 5 c.c. of sulphuric acid, heated to 100°, and titrated with decinormal potassium permanganate solution, an excess of the latter being used, and finally determined by means of standard oxalic acid. The results obtained by the authors are satisfactory. J. W. L.

The Chemical Detection of Glycosuria. By A. JOLLES (*Chem. Centr.*, 1890, ii, 609—610; from *Internat. klin. Rundschau*, 1890, Nos. 31, 32).—The author considers that a sharp distinction exists between glycotic and diabetic urines. The former contain but mere traces of sugar, about 0·4—0·5 per cent., and otherwise are not characterised by abnormal chemical and physical properties. The diabetic urines, on the other hand, have a high density, a pale-yellow colour, a less quantity of uric acid than normal urine, and contain acetone or acetoacetic acid, or acetic acid. Sugar usually occurs in them in considerable quantities, although this is not always the case. A new method, namely, to paint a visiting card first with copper sulphate solution and, after drying, to apply the suspected urine with a match, dry and heat, which has recently been proposed by v. Becker, is considered wholly untrustworthy by the author. Trommer's method, and Seegen's modification of the same, are also considered valueless by the author. Böttger's bismuth reagent and Fischer and Jaksch's phenylhydrazine test are found by him to be trustworthy.

With Böttger's bismuth reagent, 0·08 per cent. of sugar may be detected, and if the urine be first boiled with a solution of sodium chloride the delicacy is heightened, 0·01 per cent. being then detectable. At least 50 c.c. of urine must be employed to 5 c.c. of Nylander's reagent, and should not be boiled for more than two minutes. The presence of such substances as rhubarb, kairine, oil of turpentine, quinine, arsenious and salicylic acids, sulphur, mercury salts, and iodides should be avoided. In the case of considerable quantities of uric acid, it is to be observed that the brown coloration produced by it remains constant, whereas that produced by the presence of sugar becomes continually darker.

The phenylhydrazine test enables 0·015—0·038 per cent. of sugar to be detected, the delicacy being the greater the less the amount of reducible substances present. At the same time crystals, very similar to those of phenylglucosazone, are formed with glycuronic acid. The latter are, however, not so fine, and have not the same striated arrangement as those of phenylglucosazone. J. W. L.

Test for Resorcinol and Thymol. By H. BORNTRÄGER (*Zeit. anal. Chem.*, **29**, 572).—When treated in warm acid solutions with nascent nitrous acid, resorcinol gives a blood-red colour, thymol a yellowish-red. If aqueous solutions are used, that of resorcinol remains clear, whilst that of thymol gives a flocculent precipitate; alcoholic solutions remain clear in both cases. Very minute quantities can be detected and distinguished by operating as follows:—About equal quantities of a nitrite, solid gypsum, and sodium hydrogen sulphate are mixed in a test tube, and moistened with water; the liquid to be tested is added, and the whole is warmed. Thymol produces a chrome-red colour and resorcinol a dark chrome-green, magenta-red drops separating in the upper part of the tube. M. J. S.

Estimation of Acetone. By F. COLLISCHONN (*Zeit. anal. Chem.*, **29**, 562—572).—Messinger's method (Abstr., 1889, 313) is both more rapid and more exact than that of Krämer (Abstr., 1880, 826; see also Hintz, Abstr., 1888, 759). By attention to the following considerations, results of almost theoretical accuracy can be obtained. The formation of iodoform from acetone is actually effected by the alkaline hypoiodite (M′IO) which is the first product of the reaction of iodine with an alkaline hydroxide. Since, however, the hypoiodite rapidly passes into a mixture of iodate and iodide, which has no action on acetone, it is important to shake well the mixture of acetone and alkali during the addition of the iodine. If this is done, the quantity of iodine to be added need be only one-sixth more than the theoretical amount, but if it is neglected, a much larger quantity of iodine is necessary. The time prescribed by Messinger (15—30 seconds) is insufficient at low temperatures, except when the excess of iodine is large. Four or five minutes' shaking is enough in the cold, but two minutes will suffice if the mixture is warmed to 60—70°. The temperature must not exceed 70°, and the mixture must be recooled before acidifying. In presence of methyl alcohol, warming must be avoided. The degree of dilution of the acetone is unimportant, but 1 per cent. is suggested as convenient. The error due to nitrites in the alkali, for which Messinger found it necessary to make a correction, may be avoided by using soda, which can be obtained free from nitrites. M. J. S.

Estimation of Acetone in Urine. By H. HUPPERT (*Zeit. anal. Chem.*, **29**, 632).—Messinger's method (Abstr., 1889, 313; also preceding abstract) may be used, but the acetone must be distilled from the urine, and be free from phenol, ammonia, and nitrous

acid. To this end, the urine (100 c.c.) should first be distilled with 2 c.c. of pure 50 per cent. acetic acid, and then with 1 c.c. of dilute sulphuric acid, and, if nitrous acid is present, a third time with some urea.
M. J. S.

Estimation of Hydrogen Potassium Tartrate, Free Tartaric Acid, and Malic Acid and Mineral Salts in Wine. By M. SCHNEIDER (*Chem. Centr.*, 1890, ii, 277—278; from *Mitt. pharm. Inst. Erlangen*, 1890, 57—92).—The author considers that the hydrogen potassium tartrate in wine is completely precipitated by concentration and treatment with alcohol, but that it is accompanied by other salts, such as phosphates, and that the tartrate thus separated must be incinerated, and the carbonic anhydride in the ash determined, from which the amount of the tartrate may be calculated.

The following method is recommended by him :—100 c.c. of wine is evaporated, with the addition of sand, to a thin syrup, which is transferred, finally by the aid of small quantities of 96 per cent. alcohol, to a flask, and sufficient alcohol added to make up the volume of the latter to 200 c.c.; the flask is then closed and allowed to remain for 12 hours in a cool place. The solution is filtered, and the insoluble portion washed with alcohol until the washings are neutral. The filter with its contents is returned to the flask and digested with hot water, filtered, and the filtrate exactly neutralised with decinormal alkali: it is then evaporated to dryness and the residue incinerated. The carbonic anhydride in the latter is equivalent to half the quantity of hydrogen potassium tartrate in the wine. From the filtrate, the alcohol is evaporated, and 0·5 c.c. of potassium acetate (20 per cent. rendered acid with acetic acid) added, whereby the formation of hydrogen potassium tartrate is facilitated. It is then evaporated with sand, treated with 96 per cent. alcohol (200 c.c.), and the amount of acid tartrate determined as above. The carbonic anhydride contained in the ash is equivalent to the free tartaric acid present in the wine.

For the estimation of the malic acid, 100 c.c. of the wine is exactly neutralised with decinormal alkali, evaporated to dryness, incinerated, and the carbonic anhydride estimated. From this, is deducted the quantity equivalent to the tartaric acid and hydrogen potassium tartrate, the remainder being equivalent to the malic acid. The author considers that the acids and bases are combined in wine in the following manner :—The potassium is present as hydrogen potassium tartrate; the sodium as chloride; calcium as sulphate and acid phosphate; magnesium as tertiary phosphate; and iron as phosphate.
J. W. L.

Estimation of Malic Acid in Wine. By M. SCHNEIDER (*Chem. Centr.*, 1890, ii, 278—279; from *Pharm. Centralhalle*, **31**, 406—407).—Replying to a criticism of Niederhäuser (this vol., p. 128) on the author's method for determining malic acid in wine, the author contends that the amounts of tannin and succinic acid are rarely worth noticing, but that in applying the method described in the foregoing abstract, the amount of carbonic anhydride which corresponds with the volatile acids must be deducted.
J. W. L.

Analysis of Tartar and Wine Lees. By B. PHILIPS and Co. (*Zeit. anal. Chem.*, **29**, 577—579; see Abstr., 1889, 657).—To estimate the total tartaric acid, 10 grams of the substance is boiled with 150 c.c. of water and 7 grams of potassium carbonate for 30 minutes. To estimate that as potassium hydrogen tartrate alone, the potassium carbonate is omitted, and the solution accurately neutralised with sodium hydroxide. This leaves the calcium tartrate undecomposed. In either case, the whole is made up to 200 c.c. (203 c.c. for lees) and 100 c.c. of the filtrate is evaporated to 25 c.c., then mixed with 5 c.c. of glacial acetic acid and warmed for 15 minutes on the water-bath. After cooling, 100 c.c. of absolute alcohol is added, the mixture vigorously stirred, and after 15 minutes filtered by suction through a filter of 10 cm. diameter. The precipitate is washed with 96 per cent. alcohol, until 20 c.c. of the washings, diluted with an equal bulk of water, is rendered alkaline by three drops of N/5 alkali. The filter, with the precipitate, is returned to the basin, boiled with 200 c.c. of water, and titrated with N/2 alkali. The mixture should be well boiled just before reaching neutrality, and the addition of the alkali continued until a distinct excess is shown by sensitive, neutral tint, litmus paper.

M. J. S.

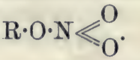
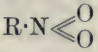
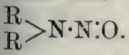
Estimation of Caffeïne in Tea. By F. VITÉ (*Chem. Centr.*, 1890, ii, 274—275; from *Mitt. pharm. Inst. Erlangen*, 1890, 113—143).—Of several methods for the estimation of caffeïne, the author has found those of Hilger (*Ziemssen-Pettenkoffer*, *Handb. f. Hyg.* **1**, 278) and of Schimoyama (*Orig. Arb. über Japanische Theekultur*) give the most trustworthy results. He recommends that of Hilger, since the caffeïne obtained is in the purest condition, and he applies it in the following form:—5 grams of tea, pulverised and passed through a hair sieve of 4 c. mm. mesh is extracted three times for one hour with 300 c.c. of water; the extract is then concentrated to one-fourth the volume and treated with freshly precipitated lead oxide with addition of sand. The mixture is evaporated to dryness on the water-bath, the residue extracted during three hours with chloroform, the latter distilled off, and the residue extracted with hot water. This aqueous extract may then be evaporated to dryness in a weighed dish, and the residual caffeïne dried at 100° and weighed. The author has employed a sieve to contain the tea during the extraction.

J. W. L.

Detection of the Colouring Matter of Alkanna Root. By A. BUJARD and A. KLINGER (*Zeit. ang. Chem.*, 1890, 26—27).—From an ammoniacal solution, ether extracts the alkanna red. In this respect it resembles orchil, but differs from the colouring matters contained in logwood, Brazil wood, bilberries, elderberries, grapes, &c. The alcoholic solution is turned red by acetic acid, and then gives a well-defined absorption spectrum of three bands, of which the first is near and on the more refrangible side of D, the second commences at E and extends beyond *b*, and the third, which is faint, is close to F. On rendering the solution alkaline by soda, it turns blue, and then shows two bands, of which one is about midway between C and D, and the other, of about equal width, commences at D. M. J. S.

General and Physical Chemistry.

Molecular Refraction of Substances containing Nitrogen. By R. Loewenherz (*Zeit. physikal. Chem.*, **6**, 552—563).—The author has measured the refractive indices n_D and n_C of a number of organic compounds, and compared the observed molecular refraction with that calculated. The molecular refractions were obtained from both the formulæ $M(n-1)/d$, in which $n = n_C$, and $M(n^2-1)/d(n^2+2)$, in which $n = n_D$, and the numbers used in calculating the refractions in the two cases were $C = 5{\cdot}0$ and $2{\cdot}501$, double linkage $= 2{\cdot}4$ and $1{\cdot}707$, $H = 1{\cdot}3$ and $1{\cdot}051$, $O' = 2{\cdot}8$ and $1{\cdot}521$, $O'' = 3{\cdot}4$ and $2{\cdot}287$. The values taken for nitrogen itself were those of Brühl, 5·75 and 2·900, but the results were afterwards used for calculating the atomic refraction of nitrogen.

Four amines were examined, diethylamine, dipropylamine, diisobutylamine, and diisoamylamine. The calculated values for the atomic refraction of nitrogen obtained from these compounds were 5·67 and 2·781. Four nitrates also were examined, ethyl, propyl, isobutyl, and amyl nitrate. Two constitutions are possible for these compounds $\mathrm{R{\cdot}O{\cdot}N}<\overset{\mathrm{O}}{\underset{\mathrm{O}}{|}}$ and  $\mathrm{R{\cdot}O{\cdot}N}\underset{\mathrm{O}}{\overset{\mathrm{O}}{\ll}}$. The numbers calculated for the first are, however, much smaller than those observed, and the second is therefore taken as the correct constitution, the numbers calculated for this being in agreement with those observed. Similar observations with nitromethane and nitroethane lead to the constitution $\mathrm{R{\cdot}O{\cdot}N{:}O}$ for these compounds, and from the examination of propyl, butyl, and amyl nitrites the constitution  $\mathrm{R{\cdot}N}\underset{\mathrm{O}}{\overset{\mathrm{O}}{\ll}}$ is derived. Dimethyl- and diethyl-nitrosamine were also examined, the constitution of these compounds being  $\overset{\mathrm{R}}{\underset{\mathrm{R}}{>}}\mathrm{N{\cdot}N{:}O}$.

From the results, it appeared that:—

1. Oxygen united by a double linkage to nitrogen has the same atomic refraction that it has when united by a double linkage to carbon.

2. Triad or pentad nitrogen united by either single or double linkage to oxygen has the same atomic refraction that is possessed by nitrogen in the amines. The mean values of the atomic refraction calculated from the above observations for the two formulæ employed are 5·38 and 2·780. H. C.

Refraction and Dispersion in Certain Metals. By H. E. J. G. du Bois and H. Rubens (*Phil. Mag.* [5], **30**, 365—378).—Thin wedge-shaped films of iron, cobalt, and nickel were deposited electrolytically. These acted as prisms, and refracted light for small angles of emission approximately according to the law of sines. The dispersion results agreed well with those of Kundt in the case of nickel, but with iron somewhat different values were found. Numerous tables and curves illustrate the paper. J. W.

Absorption Spectra of Iodine Solutions. By H. RIGOLLOT (*Compt. rend.*, **112**, 38—40).—The author has made spectroscopic and spectrophotometric observations with solutions of iodine in benzene, toluene, and metaxylene, chloroform, bromoform, the methyl, ethyl, and amyl haloïd salts, and methyl, ethyl, and amyl alcohol. For homologous compounds, and for derivatives of the same radicle, as the molecular weight of the solvent increases, the absorption band of the iodine is very slightly displaced towards the violet, and the minimum of light transmitted diminishes. C. H. B.

Gas Battery. By P. SCHARF (*Dingl. polyt. J.*, **276**, 36—40).—The author has patented a gas battery, in which it is proposed to use two gases or vapours producing a voltaic current by mutual action. He employs gases of the following groups: (1) Hydrogen, water-gas, generator-gas, coal gas, and the vapour of light hydrocarbons, such as petroleum, naphtha, or the like; (2) air, oxygen, chlorine, and fluorine. In cases where a liquid and a gas are used, the former is substituted for a gas belonging to the second group, hydrogen peroxide or nitric acid being the most suitable. The gases are prepared in separate apparatus according to the usual methods, and are collected in suitable receivers, into which they are compressed by well-known means. They are then conducted to the battery, a full description of which is given in the original paper, accompanied by detailed drawings. D. B.

Development of Electromotive Force between Mercury and an Electrolyte. By F. PASCHEN (*Ann. Phys. Chem.*, **41**, 801—832 and 899—900).—Time is required for the full development of the E.M.F. between a metal and an electrolytic solution, for a movement of the ions is necessary to effect the charge of the metallic surface, and this can only take place at a finite rate. The author by the use of dropping electrodes measures the E.M.F. between mercury and solutions of sulphuric acid, hydrochloric acid, cupric sulphate, and zinc sulphate, when the mercury is flowing at different rates. The speed of outflow may be so small that single drops are formed at the end of the capillary and fall separately through the liquid, or it may be great enough to give a continuous jet of mercury for some distance from the mouth of the tube. By measuring the length of this jet (from the capillary to the point where breaking up into drops commences), and dividing by the speed of outflow, the time is obtained during which a surface-particle of mercury is in electrical contact with the electrolyte and the electrometer simultaneously.

The results show that the mean difference of potential at a mercury surface which is increasing in size in an electrolyte does not depend so much on the nature of the increase, as on the time during which each surface-particle is in contact with the electrolytic solution. The phenomenon is to be conceived as a charging of the surface; and the mean E.M.F. at the surface is composed of those of the separate particles during the time of their contact with the electrolyte. The beginning of the charging curve is to be sought at times less than 10^{-5} seconds. The charging goes on rapidly up to 10^{-3} seconds, after which the E.M.F. increases much more slowly, the increase being very little for hydrochloric acid, considerable for sulphuric acid and the sulphates of zinc and copper. This last increase is probably due to the formation of a mercury salt on the surface. J. W.

Conductivities of Isomeric Organic Acids and their Salts. By D. BERTHELOT (*Compt. rend.*, **112**, 46—48).—Free isomeric acids usually have different conductivities, but normal salts of acids of simple function, such as maleates and fumarates, itaconates, mesaconates, and citraconates, have the same conductivities. This is true also of all the tartrates, and of the three amidobenzoates, and it is very nearly true for the three hydroxybenzoates.

Dextrogyrate tartaric acid and racemic acid have identical conductivities, and since the lævogyrate acid is identical with the dextrogyrate acid in all symmetrical properties, this result affords further proof of the dissociation of racemic acid in solution. Mesotartaric acid has a very different conductivity when in the free state.

When an excess of alkali is added to the normal salts, the equality of conductivity persists for acids of simple function, and also for amidobenzoates and the tartrates, a result which indicates that the alcoholic function of the latter is practically inoperative in very dilute solutions. Acids with a phenolic function yield salts with conductivities which are only approximately equal, and they begin to vary still more on addition of excess of alkali, the results showing that ortho-acids yield no more basic salt in dilute solutions, whilst the meta- and para-acids form polybasic salts.

If increasing quantities of acid are added to a normal salt, the results are different from those with excess of base, but the general phenomena are identical for a large number of acids. With monobasic acids, the liquid behaves simply as a mixture of the normal salt and the acid: with bibasic and polybasic acids, this does not hold good, in consequence of the existence, in the solution, of partially dissociated acid salts. Differences are observed between isomerides, such as fumaric and maleïc acids, mesotartaric acid, and the other tartaric acids. The proportions of acid salt formed are almost identical with citraconic and maleïc acids, on the one hand, and mesaconic and fumaric acids, on the other. In the case of the amidobenzoic acids, the basic function seems to be most energetic with the meta-derivative, and weakest with the ortho-derivative.

C. H. B.

Connection between the Theoretical and Empirical Isothermals of Mixtures. By A. BLÜMCKE (*Zeit. physikal. Chem.*, **6**, 153—160 and 407—410).—The theoretical and empirical isothermals of a single substance only coincide when the substance is homogeneous; if one portion is in the liquid and another in the gaseous state, the two curves are dissimilar. Van der Waals has investigated the isothermals of a mixture, and has shown how to find the empirical isothermals when the theoretical curves for all compositions of the mixture are known (*Zeit. physikal. Chem.*, **5**, 133). The author seeks to arrive at the connection more directly, and treats in the first of the above papers a mixture of two substances, extending his mode of treatment in the second paper to more complex mixtures.

J. W.

The Hydrogenation of Closed Chains. By F. Stohmann and C. Kleber (*J. pr. Chem.* [2], **43**, 1—21).—For the purposes of this research, the following thermochemical data have been determined; the heats of combustion are for constant pressure:—

	Heat of combustion. Cal.	Heat of formation. Cal.
Terephthalic acid, $C_8H_6O_4$	770·9	188·1
Dimethyl terephthalate, $C_{10}H_{10}O_4$	1112·7	172·3
$\Delta_{1,4}$-dihydroterephthalic acid, $C_8H_8O_4$	836·1	191·9
Dimethyl $\Delta_{1,4}$-dihydroterephthalate, $C_{10}H_{12}O_4$	1181·3	172·7
$\Delta_{1,5}$-dihydroterephthalic acid, $C_8H_8O_4$	842·7	185·3
Δ_1-tetrahydroterephthalic acid, $C_8H_{10}O_4$	882·8	214·2
Dimethyl Δ_1-tetrahydroterephthalate, $C_{10}H_{14}O_4$	1226·8	196·2
Cis-hexahydroterephthalic acid, $C_8H_{12}O_4$	928·6	237·4
Fumaroïd-hexahydroterephthalic acid, $C_8H_{12}O_4$	929·5	236·5
Dimethyl fumaroïd-hexahydroterephthalate, $C_{10}H_{16}O_4$	1273·9	218·1
Normal hexane, C_6H_{14}	991·2	55·8
α-Thiophenic acid, $C_5H_4SO_2$	591·9	85·4
Tetrahydro-α-thiophenic acid, $C_5H_8SO_2$	700·4	114·9

Details of the preparation of these compounds are given. Dimethyl Δ_1-tetrahydroterephthalate melts at 37°, not 39°, as stated by v. Baeyer (Abstr., 1889, 1178); α-thiophenic acid melts at 128·5°; propiothiënon boils at 226° (228°, corr.; Krekeler, Abstr., 1886, 539).

From the above numbers, and from those generally accepted for the thermal values of acids of the oxalic and acetic series, it is shown that the hydrogenation of compounds containing the benzene ring is accompanied by three distinct thermal changes:—(1) The first addition of H_2, as in the conversion of terephthalic acid into dihydroterephthalic acid, causes an increase in the heat of combustion amounting to 68·7 Cal.; (2) the addition of the next two hydrogen molecules, as in the conversion of dihydro- into tetrahydro-, and of tetrahydro- into hexahydro-terephthalic acid, causes an increase in the heat of combustion of 45·3 Cal. for each molecule; (3) the addition of the fourth molecule of hydrogen, which brings about the splitting open of the benzene ring, as in the conversion of hexahydroterephthalic acid into suberic acid, and the addition of the fifth molecule, which splits up the open chain into two different molecules, both cause an increase of 54·8 Cal. in the heat of combustion.

The correctness of these three figures is fully confirmed by the thermal values obtained for the successive hydrogenation of benzene into hexane, benzoic acid into heptylic acid, &c. The same three figures obtain also in the hydrogenation of compounds containing the pyridene and thiophen rings.

The agreement between the numbers 45·3 and 54·8 on the one hand, and the numbers representing the hydrogenation of compounds of the fatty series on the other hand, leads the authors to the following conclusion:—The thermal value of the hydrogenation of compounds containing the benzene and thiophen nuclei is entirely different in the first stage from what it is in the second and third stages, and in both these latter stages is in agreement with the thermal values of the hydrogenation of ordinary double-bond compounds in the fatty series (compare Horstmann, Abstr., 1888, 1069). A. G. B.

Endothermic and Exothermic Reactions of Organic Bases. By A. Colson (*Compt. rend.*, **111**, 884—886).—Piperidine displaces calcium from calcium chloride (Abstr., 1890, 1368) only when the solution of the latter contains not less than 55·5 grams per litre. Precipitation is more complete when the liquid is heated, and the precipitate consists of calcium hydroxide with small but variable quantities of calcium chloride and of the double calcium-piperidine compound described by Berthelot.

There are many other cases in which a reaction is determined by the solubilities of the products and not solely by the thermal disturbances. The formation of barium oxalate from the dissolved chloride and oxalic acid develops +5·6 Cal., and that of diisobutylamine oxalate from the dissolved hydrochloride +6·5 Cal.; the formation of the two oxalates from the bases and a solution of ammonium oxalate would develop +8·0 Cal. and +7·5 Cal. respectively, and yet diisobutylamine oxalate cannot be obtained in this way. On the contrary, ammonia displaces the amine at once from its oxalate, even at the ordinary temperature, although the change corresponds with an absorption of −10·8 Cal.

If normal diisobutylamine is added to an aqueous solution of trimethylamine (1 gram-mol. per litre), it first dissolves with an absorption of −6·6 Cal., and then the diisobutylamine separates with a further absorption of −7·0 Cal. Other amines behave like ammonia and trimethylamine in contact with dibutylamine oxalate, and give analogous endothermic reactions. In these phenomena, the coefficient of distribution of the acid between the two bases has to be taken into account. 3 mols. of triethylamine are required to displace 1 mol. of diisobutylamine from its hydrochloride, and 3 mols. of trimethylamine are required to dissolve 1 mol. of normal diisobutylamine oxalate, the solutions containing 1 gram.-mol. of base per litre.

The following experimental data are given :—

Diisobutylamine diss. + $\frac{1}{2}H_2C_2O_4$ diss. = solid salt	develops	+16·4	Cal.
Diisobutylamine liquid + $\frac{1}{2}H_2C_2O_4$ solid = solid salt	,,	+19·2	,,
Trimethylamine diss. + $\frac{1}{2}H_2C_2O_4$ diss. = diss. salt........................	,,	+9·6	,,
Trimethylamine liquid + $\frac{1}{2}H_2C_2O_4$ solid = solid salt	,,	+7·05	,,
Heat of dissolution of diisobutylamine ..	,,	+7·05	,,

C. H. B.

New Method of Investigating the Compressibility of Liquids and Gases: Results with Oxygen, Hydrogen, Nitrogen, and Air. By E. H. AMAGAT (*Compt. rend.*, **111**, 871—875).—The author has investigated the effects of pressures varying from 100 to 1000 atmospheres, at 0°, 100°, and 200°. For hydrogen, the values of *dv/dt* are practically independent of the temperature, and the coefficient of dilatation diminishes regularly as the pressure rises; whilst for nitrogen, oxygen, and air, it passes through a maximum corresponding with the pressure at which *pv* has its minimum value. The values *dp/dt* for hydrogen are practically independent of the temperature. Air and nitrogen approximate to hydrogen in their behaviour. Hydrogen seems, in fact, to represent the limit towards which all the other gases tend, and which is characterised by values of *dv/dt* and *dp/dt*, independent of the temperature, the first decreasing and the second increasing regularly as the pressure rises.

Further experiments have shown that the isothermals at pressures up to 3000 atmos., and at all temperatures, are not strictly right lines, but have a slight concavity towards the axis of the abscissæ.

C. H. B.

Dalton's Law. By B. GALITZINE (*Ann. Phys. Chem.*, **41**, 770—800).—Taking the gas equation of Clausius, $(p + \frac{a}{T(v + \beta)^2})(v - b) = RT$, as his basis, the author develops a theory of the behaviour of a mixture of two gases with respect to compression. The internal cohesion of such a gaseous mixture is first considered, it being assumed that the cohesive forces between both like and unlike molecules depend on the masses of the attracting bodies, and that they decrease with rise of temperature. No assumption is made, in the first place, as to how the attraction varies with the distance between the attracting molecules; but afterwards, the inverse second, third, and fourth powers are introduced into the formulæ obtained, and the consequences tested. It is found that the inverse square alone yields consistent results. The influence of the extension of the molecules on the pressure of the gaseous mixture is next investigated; and then follows a comparison of the theoretical numbers with the compression experiments of Andrews and other physicists on mixtures of gases. Under considerable pressures, the law of the inverse square seems no longer to hold good, the attraction being smaller than that deduced from theory.

The equations are finally applied to the critical state, and calculations of the critical temperature of mixtures of carbonic anhydride and nitrogen are found to be in satisfactory accordance with the experimental values of Andrews. (For previous paper, see Abstr., 1890, 105.) J. W.

Method for Determining the Absolute Density of a Gas. By J. JOLY (*Phil. Mag.* [5], **30**, 379—386).—The author weighs the gas in a strong copper sphere under a pressure of 20 or more atmos. A portion is then allowed to enter a volumenometer of 1—2 litres capacity at atmospheric pressure. Volume, pressure, and temperature are then read off, and the sphere with its remaining contents again weighed. Thus, all the data necessary for a density determination are obtained. The experimental error is considered by the author to affect only the fifth significant decimal. J. W.

Relation between the Boiling Points, Molecular Volumes, and Chemical Characters of Liquids. By O. MASSON (*Phil. Mag.* [5], **30**, 412—423).—The following law is formulated by the author:—If liquid compounds of the same group be compared at temperatures at which their vapour pressures are equal, the volumes occupied by unit weights will be inversely proportional to the molecular weights, and directly proportional to the absolute temperature; or, for each group at equal vapour pressure, $V_T/T =$ const., T being the absolute temperature of ebullition, and V_T the molecular volume at T°. By compounds of the same group are meant those of a hydrocarbon radicle with elements of the same natural family; for instance, ethyl chloride, bromide, and iodide. Small, but real deviations from this law occur, the bromide in most haloïd compounds, for instance, having the lowest value of the constant. Since the same relation holds good for vapours under equal pressure, it follows that different compounds of the same group are expanded equally in changing from liquid to vapour at the boiling point (compare Groshans, *Phil. Mag.* [5], **20**, 197).

In homologous series, the constant seems to increase by the same amount with each successive addition of CH_2.

Ramsay and Young have shown that $T \times dp/dt$ is a constant for closely allied substances. This law, taken in conjunction with the above relation and the thermodynamical equation $L/V - v = T \times dp/dt$, gives the result that in each group the molecular heat of vaporisation divided by the absolute temperature of ebullition is constant (compare Trouton, *Phil. Mag.* [5], **18**, 54). J. W.

Relation between the Boiling Points, Molecular Volumes, and Chemical Characters of Liquids. By S. YOUNG (*Phil. Mag.* [5], **30**, 423—427).—If V and V′ represent the molecular volumes of two liquids at "corresponding" pressures p and p', at which pressures their boiling points in the absolute scale are T and T′, then, according to Van der Waals, $V/V' = T/T' \times p'/p$. The author finds that, whilst this equation holds good in general for substances which are closely related, it shows deviations of as much as 17 per cent. from experimental results when the substances compared are not so related. J. W.

Connection between the Critical Data of Liquids and their Chemical Constitution. By E. HEILBORN (*Zeit. physikal. Chem.*, **6**, 578—585).—In this preliminary note, the author first shows how the molecular volumes at the critical temperatures may be calculated, and that, at the critical temperature, isomeric compounds have equal molecular volumes, the molecular volumes of all compounds being equal to the sum of the atomic volumes. He also shows that the critical molecular volume, the constant b of the Van der Waals' equation, is subject to similar laws, and that, from this, it follows that the critical data of liquids are purely functions of their chemical composition. H. C.

Viscosity of Liquid Carbon Compounds, and its Relation to Chemical Constitution. By R. GARTENMEISTER (*Zeit. physikal. Chem.*, **6**, 524—551).—The viscosity of a liquid is defined as the resistance of its particles to shear, and is constant for any liquid of constant temperature. It is measured by the work which is required to overcome the above resistance, this being, according to Finkener, $z = r^4\pi p/8lv - vs/8\pi gl$. In this expression, r is the radius and l the length of a capillary through which a volume v of the liquid of sp. gr. s flows under a pressure p in unit of time. The author has determined the value of z for a large number of organic compounds, by measuring the rate of flow from pipettes of suitable size. The results are given in tabular form, and the values of z/m and z/m^2, where m is the molecular weight, are also given, important relations between these values and the constitution of the compounds being established.

It is found that for any series of homologous compounds, with the exception of the acids, the values of z/m^2 are practically constant. The presence of a double linkage does not appear to exercise any marked effect on the viscosity, but for ring compounds the value of z/m^2 is greater than for open chain compounds, dipropyl and diallyl, for instance, giving the values 4·3 and 4·2, whereas benzene and ethylbenzene give 11·1 and 6·1. The influence of the presence of an hydroxyl group is very marked, for whereas the values of z/m^2 for the hydrocarbons are from 4 2 to 11·1, those for the normal alcohols lie between 54 and 63. In this respect, the following series of values is of interest: $C_3H_7{\cdot}OH = 63$, $C_3H_6(OH)_2 = 791$, and $C_6H_5(OH)_3 =$ about 10,000. The values for the isomeric benzyl alcohol and metacresol of 49 and 161 respectively are also noteworthy, as showing the much greater effect which seems to result from the introduction of the hydroxyl group into a closed chain. The above facts serve to account for the great viscosity of the carbohydrates. The viscosity of the acids is much less than that of the corresponding alcohols, but here also the presence of the hydroxyl group exercises a marked influence.

This is shown more particularly when an alcohol radicle is substituted for the hydrogen of the hydroxyl group, the viscosity of the ethereal salts being much less than that of the acids. From the low viscosity of acetoacetic acid, the author concludes that this compound does not, as indicated by Geuther's formula, contain a hydroxyl group other than that present in the carboxyl radicle.

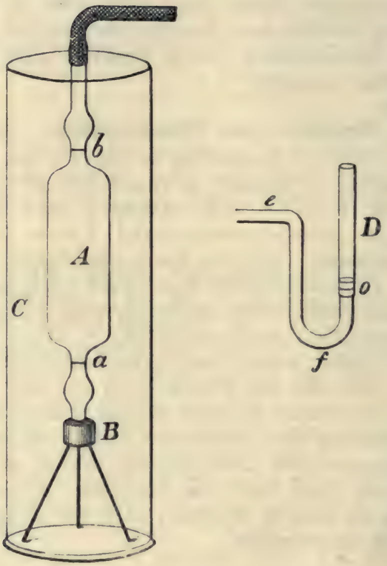
The influence of temperature on the viscosity is also studied. A decrease in the viscosity takes place with rise of temperature, this decrease becoming smaller and smaller the higher the temperature, the influence of temperature being greatest with those substances having the greatest viscosity. H. C.

Influence of Pressure on Dissociation. By B. PAWLEWSKI (*Ber.*, **23**, 3752—3755).—According to the author, the critical temperature of a mixture of liquids is calculable by the simple mixing formula $T_m = nT + (1 - n)T'$, where T and T′ are the critical temperatures of the components, n and $1 - n$ the proportions in which these are present. On this basis, one should be able to calculate the amount of dissociation of a liquid such as $C_5H_{11}Cl$ at high pressures from the observation of its critical temperature, provided those of the dissociation products (C_5H_{10} + HCl) are known. The great pressures under which the experiments must be conducted would appear to prevent the dissociation in such cases, for the observed critical temperature is much higher than that calculated from the formula, supposing the dissociation to be complete. On the other hand, with substances like $Cl{\cdot}COOC_2H_5$, which, on heating, decompose into products that have no tendency towards recombination (C_2H_5Cl + CO_2), the results of observation are in agreement with the calculated critical temperature. J. W.

Continued Dissociation and the Vapour Density of Sulphur. By E. RIECKE (*Zeit. physikal. Chem.*, **6**, 430—436).—By "continued" dissociation is meant, for example, that of a compound represented by the symbol (*abcd*), which first dissociates into (*abc*) and *d*, the molecule (*abc*) being afterwards capable of dissociating into the simpler molecules *a*, *b*, and *c*.

The author, from thermodynamical principles, deduces the mathematical law of continued dissociation, and afterwards applies it to the instance of gaseous sulphur; which, from the vapour density observations of Biltz (*Zeit. physikal. Chem.*, **2**, 920), appears to exist at the boiling point as S_8, dissociation at once taking place into S_6 and S_2, and finally entirely into S_2. A general solution of the equation applicable is impossible; but by making probable assumptions as to the form of the density curve of S_2 and of S_6, the author obtains figures which exhibit a close agreement with the numbers obtained by Biltz. J. W.

Effusion of Gases through a Narrow Aperture at Different Temperatures. By W. TIMOFÉEFF (*Zeit. physikal. Chem.*, **6**, 586—589).—The apparatus used is that shown in the accompanying sketch. *A* is a glass pipette containing 150 c.c., with small bulbs above and below, and supported by an iron tripod. *D* is a tube of copper, in which at *o* a platinum plate pierced by a narrow opening is soldered. The side tube *ef* can be connected with *A* by means of india-rubber tubing. *A* is filled with the gas to be examined and connected with *D*, the connection being, however, closed by a pinchcock. *D* is brought to the desired constant temperature, and *A* is then immersed in the cylinder of water *C*. On opening the pinchcock, water enters *A*, and the gas escapes through *o*, the time occupied by the water in rising from the mark *a* to the mark *b* being noted and giving the rate of effusion.



If c_1 and c_2 are the rates of effusion, at the temperatures t_1 and t_2, of a gas of mass m, volume v, and pressure p, the work required for the effusion of the above mass in each case will be $pv(1 + \alpha t_1) = \frac{1}{2}mc_1^2$ and $pv(1 + \alpha t_2) = \frac{1}{2}mc_2^2$. Dividing the first equation by the second, and placing $c_1 = v(1 + \alpha t_1)/z_1$ and $c_2 = v(1 + \alpha t_2)/z_2$, where z_1 and z_2 represent the time of effusion in each case, we get

$$\frac{1 + \alpha t_1}{1 + \alpha t_2} = \frac{(1 + \alpha t_1)^2}{(1 + \alpha t_2)^2} : \frac{z_1^2}{z_2^2},$$

and hence $(1 + \alpha t_1)/(1 + \alpha t_2) = z_1^2/z_2^2$ or $T_1/T_2 = z_1^2/z_2^2$, where T_1 and T_2 are the absolute temperatures. This result is of interest as it is in apparent contradiction to the deductions from the kinetic theory of gases. For since the velocity of the moving molecules increases with rising temperature, instead of a decrease in the rate of effusion at the higher temperature as indicated by the above formula, an increase might have been expected. The author's experiments with carbonic anhydride and air confirm, however, the above result, the rate of effusion becoming smaller as the temperature is raised. A quantitive test of the formula gave values for T_2 calculated as equal to $T_1z_2^2/z_1^2$, which were greater than those observed. This the author attributes to unavoidable inequalities in the aperture, which cause alterations in the area with change of temperature.

H. C.

Law of Diffusion of Liquids. By H. M. VERNON (*Chem. News*, **62**, 275—276).—Graham, in his experiments on the diffusion of aqueous solutions of various salts, did not show the existence of any general law bearing on the relations between the salts and the amounts of them diffused under similar conditions as to time, temperature, and concentration, yet several series of isomorphous salts were found to diffuse at approximately equal rates, and he endeavoured to show that the rates of diffusion of several of the different groups were to one another as the square roots of simple numbers. The author of the present note does not see why such complex relations should exist, and is of opinion that there probably is a general law for the diffusion of aqueous solutions of salts. In accordance with the kinetic theory of molecular motion, solutions of the same density should have equal rates of diffusion supposing no combination takes place between the solvent and the substance dissolved, then in a series of salts arranged regularly according to the densities of their solutions, the amounts of salts diffused ought to vary regularly from one end of the series to the other. The author has arranged two such series from Graham's numbers, reducing all to a common period of eight days; for Graham tried to find numerical relations between the periods required to obtain equal amounts of diffusate in all cases; therefore his numbers were for varying periods.

The numbers taken are also for 1 per cent. solutions only in each case, as stronger solutions do not give such regular results. Disregarding the numbers for ammonium hydrogen carbonate, potassium and sodium thiosulphates, and aluminium sulphate, which were vitiated by dissociation taking place, and those for magnesium nitrate, potassium iodide, silver nitrate, and barium chloride, which were abnormal for some reason, the diffusion values for potassium, sodium, ammonium, magnesium, manganese, calcium, zinc, and copper chlorides, potassium and sodium bromides, chromates, carbonates, sulphites, sodium iodide, potassium, sodium, magnesium, zinc, and hydrogen sulphates, and sodium, copper, strontium, calcium, and barium nitrates are shown to decrease more or less regularly with the increasing density of the solutions, and it is inferred "that solutions of the same density have equal rates of diffusion, or that with solutions of varying density, the rate of diffusion decreases regularly with increase in density of the solutions." Hydrochloric acid, nitric acid, and sodium and potassium hydroxides gave diffusion values very much greater than the normal, and so were not included in the tables.

D. A. L.

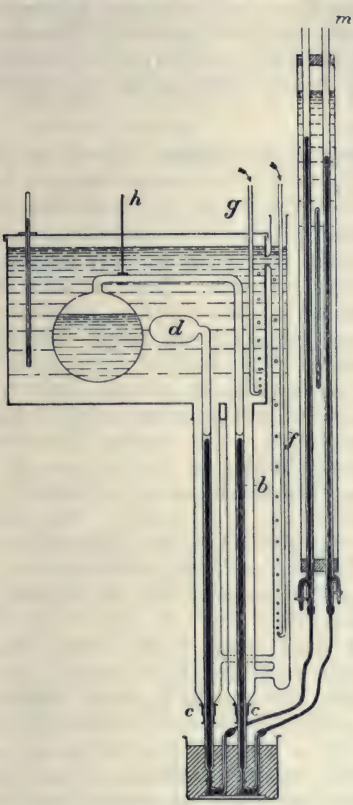
Hydrodiffusion. By O. WIEDEBURG (*Ann. Phys. Chem.*, **41**, 675—711).—The author completely fills a small glass cylinder with a salt solution of known concentration, places it inside a much larger vessel, and then carefully fills up the latter with pure water. After the diffusion has proceeded far enough, the liquid in the larger vessel is slowly run off, and the contents of the small cylinder are then analysed photometrically. The experimental results are contained in numerous tables, and the mathematical theory of diffusion for the above arrangement developed. J. W.

Evaporation and Dissolution considered as Processes of Diffusion. By J. STEFAN (*Ann. Phys. Chem.*, **41**, 725—747).—Experiments were formerly made by the author (*Wien. Ber.*, **68**, 2 Abth., 385), on the evaporation of various liquids from tubes of 1—6 mm. diameter. Two simple laws regulating the evaporation were discovered:—(1) the speed of evaporation is inversely proportional to the distance of the liquid surface from the top of the tube; (2) the speed is independent of the section of the tube. These two laws were found to be direct consequences of the theory of gaseous diffusion applied to the above process. The author now describes a parallel experiment made on the dissolution of a solid instead of the evaporation of a liquid. A rectangular prism of rock salt was enclosed on all sides (except one end) by glass plates fastened on by means of Canada balsam. This prism was placed in an upright position in a capacious vessel containing water, and the rate at which the salt dissolved was observed. When the uncovered end was upmost, the rate of dissolution was small and inversely proportional to the distance of the free salt surface from the top of the glass plates. When the uncovered surface was pointed downwards, solution took place much more rapidly owing to convection, and at a rate practically independent of the distance of the free surface from the edge of the plates. An experiment of the first kind can be used to calculate the coefficient of diffusion of a solid.

In the mathematical part of his paper, the author deduces the laws of evaporation and dissolution by making application of the theories of gaseous and liquid diffusion. J. W.

The Solubility of Gases in Water. By L. W. WINKLER (*Ber.*, **24**, 89—101).—The solubility was determined by shaking up a known weight of water with a known volume of gas, and measuring the gas remaining unabsorbed. The absorption apparatus consists of a large glass globe to which a long tube *b* is sealed; the inside measurement of the tube is 15 mm., and the length from below the level of the bottom of the globe to the open end about 850 mm.; the tube is graduated in millimetres. The capacity of the absorption globe is from 2 to 2½ litres; it is connected to the manometer tube *m* by an india-rubber tube. The apparatus *d* is provided in order to determine the tension of water vapour under the same conditions as those existing in the absorption globe, and is also connected with a manometer. The whole is surrounded by a water-bath which is stirred by air currents passing through *f* and *g*.

Solubility of *hydrogen* in water. The hydrogen was prepared from dilute sulphuric acid and pure zinc, and collected over mercury and a small quantity of potash. The gas so prepared was entirely without smell, and had no action on moist silver nitrate paper. On exploding 100 parts of the gas in an eudiometer with excess of oxygen, the contractions which took place were 150·00 and 150·01. The expansion coefficient of hydrogen was taken as 0·00366.



The mean values of the results were the following:—

	Temperature.	Absorption coefficient.
(1.)	0·57° C.	0·02131
(2.)	9·97 „	0·01955
(3.)	20·01 „	0·01819
(4.)	30·00 „	0·01699
(5.)	39·96 „	0·01644
(6.)	49·98 „	0·01608

The following interpolation formulæ were calculated:—

$$0\text{—}20^\circ \quad \beta = 0{\cdot}02148 - 0{\cdot}0002215t + 0{\cdot}00000285t^2.$$

$$10\text{—}30 \quad \beta = 0{\cdot}01955 - 0{\cdot}000144(t - 10) + 0{\cdot}0000008(t - 10)^2.$$

$$20\text{—}40 \quad \beta = 0{\cdot}01819 - 0{\cdot}0001525(t - 20) + 0{\cdot}00000325(t - 20)^2.$$

$$30\text{—}50 \quad \beta = 0{\cdot}01699 - 0{\cdot}0000645(t - 30) + 0{\cdot}00000095(t - 30)^2.$$

The solubility was calculated from the absorption coefficient by the formula $\beta' = \beta\frac{760 - f}{760}$ (Abstr., 1889, 936).

The absorption coefficient of hydrogen decreases with rise of temperature and becomes constant about 60°. Bunsen found it constant between 0° and 20° within the limits of experimental error. The author's results agree fairly closely with those of Timoféeff; the latter are somewhat higher. E. C. R.

Vapour Pressures of Solutions. By F. M. Raoult (*Ann. Chim. Phys.* [6], **20**, 297—371).—In former papers (Abstr., 1887, 631; 1888, 1145; 1889, 7; 1890, 554), the author has recorded his experiments on the vapour pressures of solutions in ether, alcohol, and acetic acid; the present paper contains the results of his examination of solutions in other solvents. The method of determining the pressures was in part that described in the previous papers, but in some cases the vapour pressure was found from the boiling point of the liquid. To make this method applicable, the thermometer bulb, which must of course be placed directly in the liquid, is surrounded by a spiral of palladium wire which has been electrolytically charged with hydrogen. On heating the solution, the vapour of the liquid is generated solely on the surface of the wire, a regular ebullition results, and the thermometer is found to register a constant boiling point to within $\frac{1}{100}$ of a degree. The boiling points of the solvents used were determined under different pressures, and it was satisfactorily established that at equal distances from their boiling points under atmospheric pressure, all the liquids in question showed the same vapour pressure.

The experiments were made with a large number of different solvents, among others carbon bisulphide, acetone, amylene, and benzene. The results are similar to those obtained in the author's study of ethereal solutions (Abstr., 1888, 1145). The general law $(f - f')/f \times (n - n')/n = k$, holds good for all solutions, the values of f and f' being the vapour pressures of the pure solvent and the solution, and n and n' being the number of molecules of the solvent and of the dissolved substance present. The normal value for the constant k is 1·04, but some solutions are found to give only half this value, and in others the number is very much higher. The first series of exceptions may be explained by assuming that the molecules of the dissolved substance are double the ordinary chemical molecule, in which case n' becomes $\frac{1}{2}n'$, and therefore in dilute solution the value of k is halved. The second series of exceptions are those which occur in aqueous and acetic acid solutions. The exceptions in aqueous solution are explained by the theory of electrolytic dissociation, whereas those with acetic acid may be referred to the well-known anomalous character of acetic acid vapour at low temperatures. These results are in accordance with those found experimentally by other observers, and with the theoretical deductions of Van't Hoff.

The reduction of the vapour pressure may be used to determine the molecular weight of the dissolved substance. In this case it is best to employ the boiling point method above described, which, as the author shows, gives accurate results. The cryoscopic method is, however, recommended in preference to the above, as being simpler and more accurate. H. C.

Determination of Solubility Coefficients. By J. W. Doyer (*Zeit. physikal. Chem.*, **6**, 481—489).—If a known amount of an indifferent gas is passed through solutions of definite concentration at a fixed temperature, then the tension of the dissolved substance may be calculated from the amount of it which is carried away, assuming that the concentration remains the same during the experiment. Assume that V litres of air at the barometric pressure B and temperature t are passed through a solution with tension x and temperature T, and that g grams of the dissolved substance are removed. Then, if γ is the weight of a litre of the dissolved gas at 0° and 760 mm.,

$$g = \gamma \frac{1}{1 + \alpha T} \times \frac{x}{760} \times \frac{V(1 + \alpha T)B}{(1 + \alpha t)(B - x - W_{T-t})},$$

where W_{T-t} is the difference between the pressure of the water vapour at T° and at t°. From this

$$x = (B - W_{T-t}) \Big/ \left\{ 1 + BV \Big/ \frac{760}{\gamma} g(1 + \alpha t) \right\}.$$

The experiments practically may be carried out in the apparatus described by Will and Bredig (Abstr., 1889, 820). Preliminary experiments with ammonia and some of the amines led to the following results for the values of x in normal solutions, calculated from experiments with solutions of different concentrations on the assumption that the tension is proportional to the concentration: ammonia, 53·7; methylamine, 40·6; dimethylamine, 90·3; ethylamine, 64·5; diethylamine, 233; propylamine, 89. The results are expressed in millimetres of mercury. The temperature of the air was 15°, that of the solution 60°. From these numbers, Ostwald's solubility coefficient, the number expressing the ratio between the concentration of the gas within and without the solutions, may be calculated, as also Bunsen's absorption coefficient. The first is equal to V/v, the second to $V/v(1 + \alpha t)$, V being the volume of the gas which is dissolved in the volume v of the solution. For the above substances we have—

	NH_3.	NH_2Me.	$NHMe_2$.	NH_2Et.	$NHEt_2$.	NH_2Pr.
Solubility coefficient..	386	511	30	321	89	233
Absorption coefficient.	316	419	188	263	73	191

The solubility coefficient is independent of the concentration of the solution, as required by the law of Henry, and the correctness of the experimental method is in so far confirmed. Former experiments of Sims gave 381 as the solubility coefficient of ammonia at 60°, a number with which the author's is sufficiently in agreement.

The author proposes to employ the above method for further investigations on solubility coefficients. H. C.

Augmented Solubility. By M. LE BLANC and A. A. NOYES (*Zeit. physikal. Chem.*, **6**, 385—402).—From the law of mass-action, taken in conjunction with the theory of electrolytic dissociation, it has been deduced by Nernst that the solubility of an electrolyte in water should be diminished by the addition to its solution of another electrolyte containing one ion in common with the first. This conclusion has been experimentally verified by Noyes (this vol., p. 142) in a considerable number of instances; but there are several well-known cases of *augmented* solubility that appear to contradict the theory. The present paper contains an account of the cryoscopic and electrolytic behaviour of some of these apparently exceptional solutions.

The solubility of lead nitrate in a solution of potassium nitrate is greater than its solubility in pure water, and *vice versâ*. This anomaly was attributed by the authors to the formation of compound molecules, and therefore a number of freezing point determinations of various solutions containing the salts in different proportions were made, in order to throw some light on the number of molecules of dissolved substance present. It was found that the addition of lead nitrate to solutions of potassium nitrate depressed the freezing point by less than the normal amount, as judged by the behaviour of corresponding solutions of sodium nitrate, which are normal in respect of their solubility in water and in solutions of lead nitrate. This result points to the formation in solution of compound molecules of lead nitrate with potassium nitrate. The latter salt by itself would seem inclined to form double molecules, for its molecular depression is much less than that of sodium nitrate. Strontium nitrate with the alkaline nitrates gives results similar to those given by lead nitrate, as far as freezing points are concerned, so that it might be expected that it would be more soluble in potassium nitrate solution than in water alone. This the authors found to be the case.

Other instances of augmented solubility investigated were: mercuric chloride in solutions of hydrogen, sodium and potassium chlorides; silver cyanide in solution of potassium cyanide; and iodine in potassium iodide solution. In all these cases the results obtained clearly indicated the existence of compound molecules in solution; and some idea of the nature of the actual molecules present was obtained. A compound, $KCl,HgCl_2,H_2O$, was isolated in the course of the investigation. J. W.

Cryohydrates of Mixtures of Salts. By D. MAZZOTTO (*Chem. Centr.*, 1890, ii, 779; from *Rend. Reale Ist. Lombardo* [2], **23**, 565, 633).—The author's investigations include the determination of the freezing points of saturated solutions of the chlorides, nitrates, and sulphates of potassium, sodium, and ammonium, and of the temperatures at which the so-called cryohydrates separate. The temperatures were determined by means of mercurial, alcoholic, and air thermometers, the last of which was one specially constructed by the author. The lowest temperature employed (−31·4°) was obtained by a mixture of sodium chloride and ammonium nitrate, or sodium nitrate and ammonium chloride. The tempera-

ture at which a cryohydrate of two salts was precipitated, was always lower than the freezing point of the saturated solution of either separately, and was approximately equal to the sum of the depression of the freezing points of the individual salts. In mixtures of two salts which contain different acids and bases, only those are capable of forming a saturated solution which contain that salt, which, of the four formed from the combination of both acids and bases under the existing conditions of the experiment, is the least soluble. The others are unstable, that is, they exchange their radicles during cooling. The author's experiments support Nernst's statements (Abstr., 1890, 3) on the mutual influences of the solubility of salts.
J. W. L.

New Application of the Cryoscopic Method to the determination of Molecular Weights. By W. NERNST (*Zeit. physikal. Chem.*, **6**, 573—577).—In a former paper (Abstr., 1890, 1368), the author showed how, when the solubility of a liquid in any solvent was decreased by the presence of some third substance soluble in the liquid but not in the solvent, the freezing point of the original solution was raised, and that this raising of the freezing point could be used in molecular weight determinations. As then pointed out, solutions of ether in water are suitable for such determinations, and in the present paper a number of new determinations with such solutions are recorded which demonstrate the great accuracy of the method. It is, of course, necessary that the substance taken should be quite insoluble in the water, otherwise greater values than the theoretical will be obtained.
H. C.

Determination of Molecular Weights by the Ebullition Method. By E. BECKMANN (*Zeit. physikal. Chem.* **6**, 437—473).—The apparatus employed has already been described by the author (Abstr., 1889, 933). The present paper contains his experimental results presented in numerous tables and curves. Benzene, chloroform, and carbon bisulphide as solvents give normal numbers for the hydrocarbons, carbonyl compounds, and ethereal salts; but for acids they yield results which point to a dissociation of double molecules. In acetic acid or alcohol, the acids have the normal molecular weight. Ethyl acetate, ethyl ether, and acetone give normal numbers, increasing somewhat with the strength of the solution, as is usually the case. The values for cadmium iodide in aqueous solution scarcely vary at all with the concentration; those for mercuric chloride, on the other hand, increase rapidly with it.

Tables of the molecular elevation of the solvents at different temperatures are given, and also a table of the elevation caused by solution of one gram-molecule in 100 c.c. of solvent. The author especially recommends the use of ether as solvent.

J. W.

Osmotic Pressure from the Standpoint of the Kinetic Theory of Gases. By L. BOLTZMANN (*Zeit. physikal. Chem.*, **6**, 474—480).—The author considers a cylinder closed at each end by a piston, and divided in the middle by a semipermeable septum. In one compartment is contained a dilute solution, the solvent of which alone can pass through the septum; the other compartment contains the pure solvent. The pressures on the pistons are adjusted so as to produce equilibrium. This system is treated, with respect to the forces in play between the different parts, after the manner adopted in the kinetic theory of gases. It is found in this way that the resultant of all the forces in the two compartments producing pressure on the septum, that is, the osmotic pressure, is equal to the gaseous pressure which the dissolved substance would exercise were it distributed as a gas throughout the volume occupied by the solution, provided that the mean kinetic energy of a dissolved molecule is assumed to be equal to that of a gas molecule at the same temperature.

The author also discusses the phenomenon of diffusion in liquids from the same point of view. J. W.

The Molecular Theory and Electrolytic Dissociation. By G. Ciamician (*Zeit. physikal. Chem.*, **6**, 403—406).—The author, reasoning from the generally accepted ideas of the nature of molecules in the various states of aggregation, seeks to show that we might expect dissociation of salts (together with powerful acids and bases) into their ions in aqueous or alcoholic solution, and in the liquid state. J. W.

The Association Hypothesis in its Relation to the Theories of Clausius and Van't Hoff. By J. Traube (*Ber.*, **23**, 3582—3589).—The dissociation theory of Arrhenius has been criticised by the author in a former paper (this vol., p. 255). For this theory he now proposes to substitute another, the association hypothesis, which is based, not on the decomposition of simple molecules, but rather of molecular aggregates (compare Armstrong, Trans., 1888, 116). To bring such a hypothesis into accordance with Clausius's theory of electrolytic conduction, he considers it sufficient to assume that double and more complex molecules take no part in conveying the current. He illustrates his theory by the discussion of the behaviour of a double molecule $(KCl)_2$, and adduces the existing evidence in favour of the assumption of complex molecules in pure liquids and in solution. The validity of Avogadro's law for dilute solutions he would still consider an open question. J. W.

Concordance in Atomic Weight Determinations. By F. W. Clarke (*Amer. Chem. J.*, **13**, 34—37).—Partridge, in his recent determination of the atomic weight of cadmium (this vol., p. 399), does not state the values he assumed for the atomic weights of carbon and sulphur in his calculations. Working back from his figures, the author finds the numbers taken were 12 and 32 respectively, which numbers gave as a mean, $Cd = 111·8015$, with the extreme range from lowest to highest result of only 0·075. If, however, the weights adopted by Stas, $C = 12·005$ and $S = 32·074$, be taken, the different values for cadmium, calculated from Partridge's three series of experiments, vary by nearly one-fourth of a unit, the small variations in the low atomic weights being multiplied in the higher figure. On the other hand, if O = 16 be taken as the standard of comparison, and the symbols of the elements carbon and sulphur are used algebraically to represent their atomic weights, the numbers obtained in the three series of experiments may be respectively transformed into the three linear equations:—

$$
\begin{aligned}
&\text{(i.)}\ 36{\cdot}036\ \mathrm{Cd} = 127{\cdot}928\ \mathrm{C} + 2493{\cdot}696,\\
&\text{(ii.)}\ 30{\cdot}801\ \mathrm{Cd} = -\ 30{\cdot}801\ \mathrm{S} + 4428{\cdot}736,\\
&\text{(iii.)}\ 28{\cdot}027\ \mathrm{Cd} = 143{\cdot}946\ \mathrm{C} - 100\ \mathrm{S} + 4606{\cdot}272,
\end{aligned}
$$

which may be solved without previously assuming the value of either, and give the numbers Cd = 111·7850, C = 11·9958, and S = 32·0002, which are independent of all errors, except those of the investigator's work, which are divided into three portions instead of being accumulated on that of cadmium (compare Strecker, *Annalen*, **59**, 280). The author suggests the desirability of attempting new determinations of atomic weights which would lie between and connect the existing data. For example, in the case of cadmium, the numbers obtained by Dumas and by Huntington, on the one hand, and Partridge, on the other, differ by half a unit; the ratios $CdO : CdSO_4$. Cd : O, Cd : S, Cd : Ag, Cd : Cl, and Cd : Br all seem to be capable of direct measurement, and would, if determined, check each other and the older values. A system of such interlacing ratios can be collectively discussed by the method of least squares, so as to distribute errors of observation, the constant error of any one series of data being equivalent to an accidental error in its relations to the other series. In a large system of ratios, the constant errors will tend to neutralise each other to a considerable degree, and would partially eliminate errors which are magnified and accumulated by the current methods of computation. G. T. M.

Sulphonation of Quinoline and Phenol. By H. FULDA (*Zeit. physikal. Chem.*, **6**, 490—523).—The object of the experiments detailed in this paper was that of studying other cases of non-reversible reactions similar to that investigated by Giersbach and Kessler in the nitration of benzene (Abstr., 1889, 10). The sulphonation of quinoline was effected with fuming acid of varying concentrations, an acid containing no anhydride having no action on quinoline below 100°. In the case of phenol, a dilute acid was used, the action of the concentrated acid being too rapid. Both changes were studied as time reactions. The results obtained were very similar to those in the case of the nitration of benzene above mentioned. Quinoline and phenol exercise a retarding influence on the reaction between these substances and sulphuric acid similar in effect to that of the benzene in its reaction with nitric acid. Hence the simple laws of mass action do not apply to these cases, the reaction being complicated by other factors, these being probably the amount of sulphonic acid and of water formed. The course of the reaction in the case of the fuming acid is a perfectly similar one to that with the dilute acid. With the fuming acid, the anhydride alone is the active agent, the sulphuric acid serving only as a diluent, that is to say, it has the same function that water has in the case of the dilute acid. H. C.

Inorganic Chemistry.

Hydrogen. By J. A. WANKLYN and W. J. COOPER (*Phil. Mag.* [5], **30**, 431–433).—The passivity of hydrogen gas is illustrated by its remaining unaltered in presence of solutions of the following substances at the ordinary temperature:—Ferric chloride, platinic chloride, potassium ferricyanide, nitric acid (sp. gr. 1·42) with or without strong sulphuric acid, aqua regia, and chromic acid. Potassium permanganate solution, on the other hand, whether it be alkaline, acid, or neutral, is attacked by hydrogen at the ordinary temperature.

J. W.

Purification of Iodine from Chlorine. By F. MUSSET (*Zeit. anal. Chem.*, **30**, 45).—The iodine is fused beneath a solution of potassium iodide sufficiently concentrated not to boil at the temperature employed. After crushing, draining, and washing, it is free from chlorine. The same solution may be used repeatedly.

M. J. S.

Utilisation of Atmospheric Oxygen. By G. KASSNER (*Dingl. polyt. J.*, **278**, 468—478).—The present paper is a continuation of a previous communication (*ibid.*, **274**, 136) in which the author described a new process for the utilisation of atmospheric oxygen and the compounds on which the process is based.

With regard to the preparation of the calcium plumbate, further investigations have shown that, instead of heating two equivalents of calcium carbonate and one of lead oxide, it is preferable to use a slight excess of the former, say about 5 per cent. In this way, a spongy product is obtained which admits of the conversion of nearly the whole of the lead oxide into plumbate. It is more advantageous to employ limestone instead of whiting, and it has also been found unnecessary to use mechanical contrivances for keeping the mixture in the form of a powder during the heating operation. This may be effected in an ordinary or reverberatory furnace supplied with a good current of atmospheric oxygen. For the production of oxygen on a large scale, the author now recommends heating the calcium plumbate in an ordinary furnace in the presence of carbonic anhydride, when oxygen is freely given off according to the following equation:—$Ca_2PbO_4 + 2CO_2 = 2CaCO_3 + PbO + O$. It will thus be seen that by this process unlimited quantities of oxygen may be obtained from one and the same material.

The author considers his process superior to the methods of Brin and Boussingault for the following reasons:—The formation of calcium plumbate is effected in the course of a few minutes, its decomposition by means of carbonic anhydride is complete, whilst the working expenses, cost of plant, and the value of material are extremely small.

D. B.

Selenium. By O. HINSBERG (*Annalen*, **260**, 40—52).—As selenious anhydride combines readily with aromatic orthodiamines with elimination of 2 mols. of water, experiments have been made in order to ascertain whether it behaves like an orthodiketone in other reactions; it has been found, however, that it has no other properties in common with ketones.

Selenious anhydride dissolves freely in hot acetic acid containing water, and, on cooling the solution, selenious acid is deposited in crystals having the composition H_2SeO_3. It is only sparingly soluble in boiling acetic anhydride, from which it crystallises unchanged, but when heated with acetic anhydride at 180—200°, it is reduced to selenium, the anhydride being oxidised to carbonic anhydride and other compounds. When a solution of selenious anhydride in 96 per cent. alcohol is evaporated over sulphuric acid, there remains a syrup which slowly loses water and alcohol, leaving a residue of selenious anhydride. If, however, an absolute alcoholic solution of selenious anhydride is evaporated over calcium chloride, large, transparent, quadratic plates, having the composition SeO_2,C_2H_6O, are deposited; these crystals lose their alcohol over sulphuric acid.

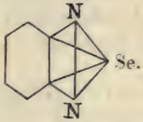
When selenious anhydride is treated with phenylhydrazine or with phenylhydrazinesulphonic acid under various conditions, it is reduced to selenium; hydroxylamine has the same action. Selenium tetrachloride reacts energetically with phenylhydrazine in benzene solution, the products being selenium, phenylhydrazine hydrochloride, and a thick, liquid oxidation product of the hydrazine.

A crystalline compound, which is probably impure *selenious cyanide*, $Se_2(CN)_2$, is formed when powdered selenious anhydride (1 mol.) is heated at 100° with anhydrous hydrogen cyanide (about 6 mols.) and acetic anhydride (2 to 3 mols.) in sealed tubes until solution is complete. On evaporating the solution over potassium hydroxide, the product is deposited in yellowish crystals which, under the microscope, are seen to consist of brownish plates mixed with a few needle-shaped crystals; the two kinds of crystals could not be separated. It is readily decomposed by warm alcohol, water, dilute acids, and alkalis, yielding selenium, selenious acid, and hydrocyanic acid or a cyanide; it has an intensely disagreeable smell, and its vapours are very poisonous.

Aniline selenite, $H_2SeO_3,C_6H_5{\cdot}NH_2$, is precipitated in crystals when an absolute alcoholic solution of selenious anhydride (1 mol.) is mixed with an ethereal solution of aniline (2 mols.) and then a little water added; it crystallises from water, in which it is readily soluble, in colourless needles, and melts at 95°. It is completely decomposed by water at 100—110°, yielding an amorphous, dark-blue substance which contains selenium, carbon, hydrogen, and nitrogen, and is insoluble in all solvents except concentrated sulphuric acid, from which it is reprecipitated on the addition of water.

Selenious anhydride seems not to combine with carbamide, but it reacts readily with phenyl mercaptide, yielding phenyl bisulphide and a selenium compound, the nature of which could not be determined.

The author is of the opinion that, in order to account for the stability of piaselenole derivatives, it must be assumed that the piaselenole nucleus has the constitution



F. S. K.

The Discovery of Nitrogen Hydride, Azoimide. By D. MENDELÉEFF (*Ber.*, **23**, 3464—3472).—The preparation of nitrogen hydride, azoimide (Curtius, this vol., p 56), and the preparation of nickel carbon monoxide (Mond, Langer, and Quincke, Trans., 1890, 749) must be ranked amongst the most important chemical discoveries of last year. Although the author never published any statement with reference to the compound recently described by Curtius, the possibility of its existence was nevertheless foreseen by him, in consequence of certain views he held regarding nitriles, these views having been advanced in a paper communicated to the first congress of Russian naturalists in 1867, and also in his *Principles of Chemistry* (1868—1870).

The publication of these views at the present time may, perhaps, help to explain the structure of nitrogen hydride, and to indicate its position among the other known compounds of nitrogen, possibly also to point out reactions and new methods by which this interesting acid may be prepared, and in this way throw some light on the nature of the metallic compounds of nitrogen.

When an element R combines with univalent elements X, to form a compound of the formula RX_n, the corresponding salt-forming hydrate has the composition $RO_{\frac{m}{2}}(OH)_{n-m}$, in which, however, the total number of oxygen atoms is never more than four; this statement is based on conclusions drawn from a study of the periodic system, in accordance with which the relationship between the composition of the hydride and that of the higher salt-forming oxides on the one hand, and between the composition of the hydrates and that of the hydrogen compounds on the other, in the case of any element, may be expressed as follows:—(1) The sum of the valencies of the hydrogen and oxygen atoms (in the highest salt-forming oxides) which can combine with any element is equal to eight; (2) the number of oxygen atoms in the highest salt-forming hydrates is four; and as a consequence of the first two conclusions (3), the greatest quantity of hydrogen in the salt-forming hydroxides is not greater than that in the hydride of the element, when the hydride is a gaseous compound of the formula RH_n.

It is evident, therefore, firstly, that an element R, which, like nitrogen, for example, forms compounds of the composition RH_3 and R_2O_5, or in general RX_3 and RX_5, cannot form a salt-forming hydrate of the formula $R(OH)_5$, although the compound $R(OH)_3$ is capable of existence. Secondly, that even the highest hydrate RH_3O_4 may lose a part of its water, forming incomplete hydrates such as $H_3PO_4 = PO(OH)_3$, $H_4P_2O_7 = [PO(OH)_2]_2O$, and $PO_2(OH)$. Thirdly, that the forms of the normal ammonium salts of any element must correspond with the hydrates of the element, and, consequently, may contain oxygen atoms other than those which unite the ammonium radicles to the element R; the compounds $NO_2(ONH_4)$, $SO_2(OH)(ONH_4)$, $CO(OH)(ONH_4)$, $CO(ONH_4)_2$, $COH(ONH_4)$, &c., may be quoted as examples of substances of this nature.

When such ammonium salts as these lose the elements of water, amides are formed in the first place by the elimination of water from the ONH_4 group; when the amides themselves lose the elements of water, a process which can only take place in the case of those derived from ammonium salts of the type given above, which contain excess of oxygen, nitriles are formed; ammonium hydrogen sulphate, for example, would first yield the amide $SO_2(OH)\cdot NH_2$, and then the nitrile SO_2HN.

Now, since nitrogen and phosphorus form the compounds NH_3 and PH_3 respectively, their highest possible hydrates are the following:—

Meta-: N_2O_5,H_2O and $P_2O_5,H_2O = 2PO(OH)_3 - 2H_2O$.
Pyro-: $N_2O_5,2H_2O$,, $P_2O_5,2H_2O = 2PO(OH)_3 - H_2O$.
Ortho-: $N_2O_5,3H_2O$ and $P_2O_5,3H_2O = 2PO(OH)_3$.

The complete hydrates, on the other hand, as, for example, $N_2O_5,5H_2O = 2N(OH)_5$, are unstable compounds, which are usually regarded simply as solutions; the ortho- and pyro-hydrates of nitric acid must also be regarded as unstable compounds, whereas the corresponding derivatives of phosphorus have long been looked on as distinct and definite hydrates, on account of the existence of the corresponding salts. As, on the other hand, in its basic mercury and lead salts, nitric acid shows a tendency to form ortho-salts, the fact that nitrogen compounds analogous to disodium hydrogen phosphate, $PO(OH)(ONa)_2$, cannot be easily produced, is simply one of the peculiarities which distinguish nitrogen from phosphorus, and which show the relative stability of phosphoric anhydride and ammonia compared with nitric anhydride and hydrogen phosphide, PH_3. It may, therefore be considered as probable that, in addition to the meta-, or ordinary, ammonium nitrate, $NO_2\cdot ONH_4$, the pyro- and ortho-compounds, or the di- and tri-ammonium nitrate,

$$NO(OH)(ONH_4)_2 \text{ and } NO(ONH_4)_3,$$

and the corresponding amido- or anhydro-derivatives $NO_2(ONH_4)NH_3$ and $NO_2(ONH_4)2NH_3$ are capable of existence. Both these anhydro-compounds have, in fact, been prepared by Divers (this Journal, 1873, 598), who considered them as solutions in which the tendency of ammonium nitrate to liquefy anhydrous ammonia is exhibited; but, in the following year, Raoult proved that the liquid produced in this way has a definite composition, $NO_2(ONH_4)2NH_3$, and that between $-10°$ and $+28°$, it is decomposed into a definite solid compound of the composition $NO_2(ONH_4)NH_3$, which, in its turn, is readily dissociated on warming with liberation of ammonia.

These compounds, then, the existence of which was rendered probable from the conclusions arrived at above, correspond with the incomplete hydrates of (ortho-, meta-, and pyro-) nitric acid, and must, therefore, to a certain extent, have an amide-like nature, in which case it is to be expected that they would be converted into nitriles by further loss of the elements of water. Assuming that the elimination of water takes place as completely as possible, then, just as ammonium nitrate is convered into the nitrile, nitrous oxide, the compound $NH_4NO_3NH_3$ would yield the nitrile N_3H, and the compound $NH_4NO_3,2NH_3$ the nitrile N_4H_4; the second of these nitriles is Curtius' nitrogen hydride, the third is its ammonium salt $N_3{\cdot}NH_4$.

As regards the properties of nitrogen hydride, which, at the first consideration, seem to be very unexpected, it can be shown that they are capable of easy explanation. The simplest, and at the same time the most plausible, view of the conversion of ammonium salts into amides and nitriles consecutively is, that, in the first place, the elements of water are eliminated solely at the expense of the ONH_4 group; it is in this way that all acid-amides are produced. When, however, the oxygen of the ONH_4 and OH groups has been taken away, any further loss of water can only take place by the combination of the hydrogen of the amido-group with the oxygen of the acid radicle, as is the case, for example, in the formation of HCN from $H{\cdot}CO{\cdot}NH_2$.

If these arguments are borne in mind in considering the formation of hydrogen nitride, it is clear that it may be regarded as derived from the di-ammonium salt of orthonitric acid,

$$NO(OH)(ONH_4)(ONH_4),$$

by the elimination of 4 mols. of water. The resulting compound NHNN contains two nitrogen atoms originally belonging to ammonium groups, and only one which belongs to the nitric acid molecule; whilst the hydrogen atom also belongs to the elements of nitric acid, and must, in consequence, possess the same character as in acids, not as in ammonia; considering also the energetic acid nature of nitric and nitrous acid, compared with carbonic acid, for example, and the position of nitrogen in the periodic system, which assigns to it more marked acid-forming properties than carbon, it follows that the nitrile, hydrogen nitride, must have a distinctly acid character. This conclusion is based on the fact that hydrogen cyanide, the nitrile of formic acid, has a distinctly acid character, notwithstanding that the hydrogen atom of the nitrile, when forming a component of the molecule of formic acid, is not replaceable by metals, and that it is subject to the influence of carbon, a feebler acid-forming element than nitrogen. The hydrogen atom in hydrogen cyanide must owe its acid character to the influence of the nitrogen and the carbon atom, and since the hydrogen atom in nitrogen hydride is in combination with nitrogen only, which is so decidedly an acid-forming element, it must have the properties of an acid.

Now, if nitrogen hydride is in reality a nitrile, it should, like the cyanogen compounds, have many peculiar properties; as, up to the present time, it has been but little investigated, it may be of interest to predict a few of the properties which, on further examination, nitrogen hydride may be found to show. It is probable, for example, that the ammonium salt $N_3 \cdot NH_4$, which seems to be an asymmetrical compound, and, to a certain extent, analogous to ammonium cyanate, will undergo intramolecular change under suitable conditions, perhaps on warming its solution, and be converted into the symmetrical amide $N(NH_2)\vdots N(NH_2)$, the amido-nitrile of triammonium orthonitrate. Again, it is probable that if nitrogen hydride should form a double salt with iron and potassium, this compound will give rise to a series of characteristic, coloured salts, which would be analogous to the salts of hydroferrocyanic acid, and also to a series of compounds of the composition Fe_nN_{3m}, corresponding with Prussian blue, which, if capable of existence in the dry state, would, doubtless, be highly explosive. As regards the capability of forming polymerides, it may be assumed that the behaviour of hydrogen nitride and its derivatives is already indicated by the behaviour of the analogous phosphorus compounds, such as chlorophosphamide, $P_3N_3Cl_6$, and phospham; the latter is probably a polymeride of the composition $(PHN_2)_n$, and not the next analogue of nitrogen hydride, and it was, in fact, a consideration of this view of its nature which led the author to foresee the existence of nitrogen hydride. F. S. K.

Preparation of Hydrogen Phosphide. By R. LÜPKE (*Chem. Centr.*, 1890, ii, 642—643; from *Zeit. f. physikal. und chem. Unterricht.*, **3**, 280—289).—Tin and zinc phosphides are prepared by adding the equivalent quantity of amorphous phosphorus to the respective metals in the molten state covered with ammonium carbonate (?). Iron phosphide, FeP, by heating finely divided iron and amorphous phosphorus together; copper phosphide, by heating copper filings with amorphous phosphorus; magnesium phosphide, by adding the equivalent quantity of amorphous phosphorus to melted magnesium; sodium phosphide, by carefully adding yellow phosphorus to fused sodium under petroleum. The phosphides of tin, zinc, iron, and copper are not decomposed by water; whilst those of sodium and magnesium, like that of calcium, are decomposed by water. From magnesium phosphide, whether decomposed by water or by dilute hydrochloric acid, non-spontaneously inflammable hydrogen phosphide is obtained. From sodium phosphide, spontaneously inflammable hydrogen phosphide is obtained, which, in a great measure, readily changes to solid phosphide. The phosphides of tin and zinc are decomposed by cold dilute hydrochloric or sulphuric acid, but those of iron and copper are but slightly attacked even on boiling.

For the preparation of hydrogen phosphide from the phosphides of tin, zinc, or magnesium, an Erlenmeyer flask of 200—300 c.c. capacity is fitted with a stopper carrying three tubes; the one conducts carbonic anhydride gas to the bottom of the flask to displace the air, the second admits the dilute acid from a tap-funnel, the third is the delivery tube. To the latter is attached a tube, filled with glass wool, from which the gas passes out into nitric acid in a dish. In the case of tin phosphide, the flask is warmed gently on the water-bath at the commencement, after which the reaction proceeds regularly for thirty minutes to one hour, when, as the reaction becomes slower, the flask may be again warmed. In the case of zinc or magnesium phosphides, no external heating is requisite. The method is preferable to the preparation with potassium hydroxide and phosphorus or to that with calcium phosphide, and demonstrates the formation of the phosphide of hydrogen in analogous manner to the other compounds of hydrogen with the non-metals, ammonia excepted. The preparation of zinc phosphide is also especially recommended as being simple. The synthesis of hydrogen phosphide may be shown by putting sodium phosphite or hypophosphite into a hydrogen generator, when the phosphide is readily detected in the gas evolved. J. W. L.

Combination of Ammonia with Phosphorus Chlorides and Bromides. By A. Besson (*Compt. rend.*, **111**, 972—974).—Phosphorus trichloride combines with dry ammonia with development of heat and formation of a white solid to which Persoz gave the formula $PCl_3,4NH_3$, and Rose the formula $PCl_3,5NH_3$. The author's analyses confirm Rose's formula.

Ammonia acts very energetically on phosphorus pentachloride with formation of a considerable quantity of ammonium chloride, resulting most probably from the partial dissociation of the pentachloride in consequence of the great development of heat. If, however, the pentachloride is dissolved in carbon tetrachloride and dry ammonia is slowly passed into the solution, care being taken to avoid elevation of temperature, a white substance separates, which is somewhat stable in air and even when heated at 200°; it has the composition $PCl_5.8NH_3$. Phosphorus pentabromide, under the same conditions, yields a compound which is precisely similar in appearance, but has the composition $PBr_3.9NH_3$.

The action of phosphorus trichloride on phosphine at the ordinary temperature produces the solid hydride P_2H, and not phosphorus as Rose stated. This reaction, in fact, affords a convenient process for the preparation of this hydride in a pure state. The reaction does not take place at $-20°$, but the trichloride absorbs a considerable quantity of phosphine, and when the liquid returns to the ordinary temperature, the solid hydride is formed. Phosphorus tribromide behaves in a similar manner, but the reaction proceeds even at $-20°$. C. H. B.

Preparation of Pure Phosphoric Acid. By M. Nicolas (*Compt. rend.*, **111**, 974—975).—Powdered calcium phosphate is added gradually to a slight excess of commercial hydrofluoric acid diluted with an equal volume of water, and contained in a leaden or platinum vessel. There is considerable development of heat, and the liquid must be thoroughly agitated. When the action moderates, the liquid is gently heated, water being added to make up for loss by evaporation. When the liquid becomes viscous, the excess of hydrogen fluoride begins to escape, and the mixture is then heated until the expulsion of the acid is complete. The syrupy liquid thus obtained contains from 60 to 70 per cent. of phosphoric anhydride in the form of orthophosphoric acid. With pure materials, the phosphoric acid obtained is very pure; if bones and ordinary acid have been used, the product must be heated to carbonise the organic matter, dissolved in water, filtered, and again evaporated. Pyrophosphoric and metaphosphoric acids can be obtained by evaporating at higher temperatures.

If hydrofluoric acid is added drop by drop to a large excess of powdered calcium phosphate, and the product is extracted with warm water, the solution, on evaporation, leaves a residue containing the various salts described by Erlenmeyer. C. H. B.

Redetermination of the Atomic Weight of Cadmium. By E. A. Partridge (*Amer. J. Sci.* [3], **40**, 377—384).—The purification of the cadmium was effected by distillation in a vacuum in tube retorts of glass, about 300 mm. in length and 20—25 mm. in diameter. About 100 grams of cadmium was distilled until 60 grams had passed over, and the distillate was again distilled until about one-half had passed over. The residue in the first distillation when examined spectroscopically was found to contain lead, iron, thallium, a little copper, and traces of zinc; the residue from the second distillation was found to be entirely free from these impurities. All the cadmium used in the investigation was purified in this manner by double distillation.

Three methods were used for determining the atomic weight.

I. Cadmium oxalate was converted into the oxide by heating. Care must be taken that the temperature does not become too high, or reduction or volatilisation of the metal takes place.

II. Cadmium sulphate was converted into sulphide by heating in a current of hydrogen sulphide. The sulphate was weighed in stoppered glass tubes to prevent the absorption of water; the hydrogen sulphide was obtained from antimony sulphide, and was therefore free from hydrogen, and it was ascertained that cadmium sulphide is non-volatile when heated.

III. Cadmium oxalate was converted into sulphide by heating in a current of hydrogen sulphide. This change takes place at a temperature much below that which is required to convert the salt into oxide.

The results obtained were as follows:—

I. Mean of 10 experiments, 111·8027. Probable error, 0·010.
II. ,, ,, 111·7969. ,, ,, 0·008.
III. ,, ,, 111·8050. ,, ,, 0·009.

Regarding each series as of equal value, the mean of the three series gives 111·8015 as the atomic weight of cadmium, with O = 16. (Compare Clarke, this vol., p. 390). H. C.

Cuprammonium Bromides. By T. W. Richards (*Ber.*, **23**, 3790—3791).—By the action of dry ammonia on cupric bromide, a blue powder is obtained, which readily loses part of its ammonia in the air, and has the composition $CuBr_2,6NH_3$, and not $CuBr_2,5NH_3$, as given by Rammelsberg (*Ann. Phys. Chem.*, **55**, 246). It corresponds therefore in composition with the chlorine compound, and may be termed *tetrammoncuprammonium bromide*. It is soluble in small quantities of water, but on dilution, cupric hydroxide separates.

On exposure to the air, it readily loses ammonia, forming an olive-green powder; this takes place even more easily on heating, the substance becoming quite green at 165° even in an atmosphere of ammonia. It then has the composition $CuBr_2,2NH_3$, and corresponds with the "apple-green" chlorine compound. It readily absorbs ammonia, again becoming blue, and may be heated to 200° without alteration, but at higher temperatures it decomposes, forming copper and ammonium bromides, &c. It dissolves in aqueous ammonium bromide without decomposition, and may seemingly be recrystallised from this liquid. Similar crystals may be obtained by cautious addition of ammonia to a mixture of cupric and ammonium bromides.

H. G. C.

Mercury Arsenates and Phosphates. By K. HAACK (*Chem. Centr.*, 1890, ii, 736—737; from *Inaug. Diss. Halle*, 1890).—*Mercuric arsenate*, $Hg_3(AsO_4)_2$, is prepared by adding a solution of mercuric nitrate to one of disodium arsenate. It is a lemon-yellow powder, very slightly soluble in water, readily soluble in hydrochloric acid, sparingly soluble in nitric acid, insoluble in arsenic acid.

Mercuric phosphate, $Hg_3(PO_4)_2$, is prepared by adding a strongly acid solution of mercuric nitrate to one of disodium phosphate. It is a white salt, neutral to litmus, readily soluble in hydrochloric acid, but insoluble in phosphoric acid. From a neutral solution of mercuric nitrate, the salt is precipitated with admixture of normal or basic mercuric nitrate.

From solutions of mercuric chloride, disodium arsenate precipitates the mercuric arsenate mixed with oxychloride. From solution of mercuric chloride, disodium phosphate causes a reddish-brown precipitate of the composition $HgCl_2 + 2HgO$, which contains a little disodium phosphate. By boiling basic mercuric sulphate with solution of disodium arsenate, a mixture of normal mercuric arsenate and mercuric oxide is formed, from which the latter may be removed by boiling acetic acid; an analogous reaction takes place with disodium phosphate. Mercuric iodide does not react with either of the sodium salts; mercuric oxide does not react either with the free acids or the salts. The double mercuric nitrate and sulphide does not react with the sodium salts in the cold, but on heating, mercuric sulphide is precipitated.

Mercurous nitrate (in excess) forms a double salt with disodium arsenate, of the formula $3Hg_3AsO_4 + 2(HgNO_3 + Hg_2O)$. If the arsenate is in excess, the normal mercurous arsenate, Hg_3AsO_4, an orange-coloured amorphous powder, is formed. With disodium phosphate, analogous compounds are produced; the double salt contains, however, basic mercurous nitrate.

For the determination of nitric acid in the presence of arsenic and phosphoric acids and mercury, these were precipitated with excess of barium hydroxide, the excess of the precipitant was then separated with carbonic anhydride, and the nitric acid calculated from the amount of barium remaining in the solution. J. W. L.

Ultramarine. By J. HEINTZE (*J. pr. Chem.* [2], **43**, 98—105).—The claim of Köttig, the director of the laboratories of the Königl.

Porzellan-Manufactur in Meissen, as a discoverer of artificial ultramarine, has been overlooked, and mention of him is omitted from chemical literature; yet Köttig's discovery occurred in the spring of 1828, which was the very time when Gmelin and Guimet were disputing as to priority. The manufacture at Meissen is now abandoned, but, as the ultramarine emanating therefrom had a higher value, and was in greater demand than many other products, the author considers that an exact description of the process of manufacture adopted at these works will prove of value. As success depends on details, it is obvious that a short abstract of the process followed would be of little value. A. G. B.

Removal of Gold from Suspension and Solution by Fungoid Growths. By A. LIVERSIDGE (*Chem. News*, **62**, 277—279, 290—291).—In various bottles of distilled water holding in suspension gold reduced from the chloride by phosphorus in ether, and which had been in the dark for years, it was observed that the gold had only settled completely in those bottles in which fungoid growths had formed, and in such cases the metallic gold was easily detected in the growths. Various experiments were instituted to investigate the matter, and a solution of sodium aurochloride was exposed in the light to the action of various growths, such as those usually met with in solutions of potassium acetate, citric acid, oxalic acid, magnesium sulphate, and potassium tartrate, also cheese and banana moulds and bread, and other organic matter, all of which not alone removed gold in suspension but also from solution. The growths do not form in the presence of carbon bisulphide, chloroform, benzene, or turpentine, neither did the oxalic acid mould thrive or act. D. A. L.

Ammoniacal Derivatives of Ruthenium Nitrosochloride. By A. JOLY (*Compt. rend.*, **111**, 969—972; compare (Abstr., 1889, 352, 678, 948).—When the chloride $OH\cdot RuCl_2,NO,4NH_3$ is mixed with a large quantity of acid and evaporated by heat, it becomes turbid and deposits a red powder, only slightly soluble in water. The product can be dissolved in boiling water, and separates in small, very dense, orange-coloured crystals of the composition $RuCl_3,NO,4NH_3$. The corresponding bromine and iodine derivatives are obtained in a similar manner. With platinum chloride, a solution of the trichloride yields a very dense, crystalline precipitate of the platinochloride, $RuCl_3,NO,4NH_3,PtCl_4$.

The strongly acid liquid from which the trichloride has separated has the colour of potassium dichromate, and when allowed to evaporate spontaneously deposits long, red or orange-red, monoclinic prisms of 105° 54′. They have the composition $RuCl_3,NO,4NH_3,2H_2O$, are very soluble in cold water, and differ from the trichloride in being acid to methyl-orange. The compound is, therefore, most probably not merely a hydrate of the trichloride, but is a hydrochloride of a hydroxy-dichloride, $OH\cdot RuCl_2,NO,4NH_3,HCl + H_2O$. When heated, it loses water and hydrogen chloride, and is partially converted into the trichloride. If the solution is evaporated, some trichloride separates, and the conversion becomes complete on evaporation to dryness. Platinum tetrachloride gives a yellow, crystalline precipitate of the platinochloride, $OH\cdot RuCl_2,NO,4NH_3,PtCl_4$.

By double decomposition with silver nitrate, the salt $RuCl_3,NO,4NH_3$ yields the nitrate $Ru(NO_3)_3,NO,4NH_3$, more soluble than the nitrate $OH\cdot Ru(NO_3)_2,NO,4NH_3$ previously described. The same product is obtained by evaporating either of the chlorides to complete dryness with excess of nitric acid. If the liquid is merely boiled with excess of the acid for some time, it becomes red, and deposits crystals of an acid salt $OH\cdot Ru(NO_3)_2,NO,4NH_3 + HNO_3$.

The sulphates are more complex, and their number is greater in consequence of the formation of acid salts and of hydrates. They all crystallise well, but some decompose readily when redissolved in water. When the trichloride or hydroxy-dichloride is evaporated with a slight excess of sulphuric acid, and the product is allowed to crystallise from the acid liquid, the acid sulphate, $(RuNO,4NH_3)_4(SO_4)_6 + H_2SO_4 + Aq$, is obtained in small yellow or orange-yellow needles. This salt decomposes in presence of a small quantity of cold water, leaving a pink residue, which dissolves with difficulty in boiling water, forming a solution which is neutral to methyl orange. When the solution cools, the salt $(RuNO,4NH_3)_2(SO_4)_3 + 10H_2O$ separates in slender, nacreous needles, but if the solution is boiled for a long time it deposits a sulphate corresponding with the hydroxy-dichloride. The sulphate, $OH\cdot RuSO_4,NO,4NH_3 + H_2O$, has previously been described; when crystallised in presence of a slight excess of sulphuric acid, it is converted into orange-red crystals of the acid sulphate,

$$OH\cdot RuSO_4,NO,4NH_3 + H_2SO_4 + Aq,$$

and this when heated is partially converted into the sulphate corresponding with the trichloride.

All these new compounds in ammoniacal solution yield the hydroxy-dichloride ($Cl_2\cdot OH$), or the corresponding sulphate or nitrate. When heated with aqueous potash, ammonia is evolved, and the nitrosohydroxide, $Ru(OH)_3,NO$, forms and dissolves in excess of alkali. When this solution is saturated with hydrogen chloride, the salt $RuCl_3,NO,2KCl$ separates. It is clear that the group NO is very intimately united to the ruthenium. C. H. B.

Iridioammonium Compounds. By W. PALMAER (*Ber.*, **23**, 3810—3819).—The author has previously shown (Abstr., 1889, 352) that three different series of iridioammonium compounds may be obtained. The present paper gives a more detailed description of those compounds containing 5 molecules of ammonia to 1 atom of iridium, which correspond with the "purpureo-" compounds of cobalt, chromium, and rhodium. As, however, the iridium derivatives are pale-yellow, the name "purpureo-" is unsuitable for them, and the term pentamine-compounds is therefore employed.

Iridiumpentamine trichloride, $Ir(NH_3)_5Cl_3$, is obtained by the action of ammonia on iridium trichloride or tetrachloride or their double salts, in the form of wine-red crystals; if it is prepared from the chlorosulphate by the action of barium chloride, the crystals obtained are yellow, the red colour of the first being due to a slight admixture of ammonium iridiochloride. Both varieties give exactly the same measurements. It crystallises in the rhombic system ($a : b : c = 0·9873 : 1 : 1·5527$), and is isomorphous with the corresponding cobalt and rhodium compounds. It has a sp. gr. of 2·68 at 15·3°, dissolves in 153·1 parts of water at 15·1°, and is not altered on heating at 275°. As with the other "purpureo-" salts, one atom of chlorine is more firmly combined than the other two, and is not removed by cold sulphuric acid or cold silver nitrate solution.

Iridiumpentamine chlorosulphate, $Ir(NH_3)_5ClSO_4 + 2H_2O$. The preparation of this salt has already been described (*loc. cit.*). If, after treating the chloride with sulphuric acid, water is added, a precipitate of slender, matted needles separates on cooling, which probably consists of the *acid sulphate*. These redissolve on warming, and the normal salt is then precipitated on the addition of alcohol. The latter forms small, strongly refractive, monosymmetric crystals ($a : b : c = 1·1984 : 1 : 0·74831$; $\beta = 84° 48\frac{1}{2}'$), has a sp. gr. of 2·551 at 15·2°, and dissolves in 134·5 parts of water at 15°.

Iridiumpentamine chlorobromide, $Ir(NH_3)_5ClBr_2$, obtained by decomposing the chlorosulphate with the theoretical quantity of barium bromide, forms pale-yellow, rhombic crystals

$$(a : b : c = 0·98765 : 1 : 1·5296),$$

dissolves in 213·6 parts of water at 15°, and has a sp. gr. of 3·007 at 16°. The *chloriodide*, $Ir(NH_3)_5ClI_2$, obtained in a similar manner, forms brownish-yellow, rhombic crystals ($a : b : c = 0·9424 : 1 : 1·4220$), soluble in 104·5 parts of water at 15°, and having a sp. gr. of 3·118 at 15·6°. The *chloronitrate*, $Ir(NH_3)_5Cl(NO_3)_2$, dissolves in 51·54 parts of water at 15°, and has a sp. gr. of 2·404 at 15·4°. The *chloronitrite*, $Ir(NH_3)_5Cl(NO_2)_2$, obtained from the trichloride by treating it with the theoretical quantity of silver nitrite, crystallises in large, pale yellow, rhombic prisms ($a : b : c = 0·9651 : 1 : 0·5350$), is readily soluble and has a sp. gr. of 2·519 at 16·8°. The *chloroxalate*, $Ir(NH_3)_5ClC_2O_4$, forms slender, white, sparingly soluble needles, and the *platinochloride*, $Ir(NH_3)_5Cl,PtCl_6$, a heavy, orange-yellow precipitate, which is very sparingly soluble in water, and consists of microscopic, almost rectangular, tablets.

A solution of the chloronitrate gives precipitates with solutions of a large number of salts, amongst which may be mentioned potassium iodide, ferrocyanide, and dichromate, ammonium oxalate, barium dithionate, and mercuric chloride. Silver nitrate and sodium phosphate give no precipitate. The solution of the trichloride gives a precipitate of the platinochloride with platinic chloride and sulphuric acid, whilst gold chloride gives a precipitate of lustrous, garnet-red, rhomboïdal prisms. Aqua regia resolves the trichloride into iridium tetrachloride and ammonium chloride, the latter being, for the most part, further decomposed; if chlorine gas be passed into the cold aqueous solution of the chloride, this assumes a colour similar to that of potassium permanganate, which disappears in daylight, the solution becoming brown. Further addition of chlorine, or shaking with alcohol and ether, renews the colour for a short time.

The above reactions agree closely with those of the corresponding cobalt, chromium, and rhodium compounds, with the exception that rhodiumpentamine trichloride is not attacked by chlorine. A further difference in the compounds of these two metals is shown in the behaviour of the chlorine atom combined directly with the metal, which is much more readily displaced in the case of the rhodium salt.

To obtain *iridiumpentamine tribromide*, $Ir(NH_3)_5Br_3$, it is necessary to heat the chloride with water and soda or silver oxide for several hours, which probably yields a mixture of the roseochloride and roseohydroxide, and to treat the product with concentrated hydrobromic acid. It forms yellow, well-developed, rhombic crystals ($a : b : c = 1·0254 : 1 : 1·6086$), dissolves in 352 parts of water at 12·5°, and has a sp. gr. of 3·246 at 16·7°. The *bromonitrite*, $Ir(NH_3)_5Br(NO_2)_2$, crystallises in thick, pale-yellow prisms, soluble in 17·9 parts of water at 18°, the solution having an alkaline reaction. Its sp. gr. is 2·733 at 13·5°. The *bromosulphate*, $Ir(NH_3)_5BrSO_4 + H_2O$, is obtained by triturating the foregoing salt with an excess of sulphuric acid. On adding water and cooling, slender, matted needles separate, which probably consist of the acid sulphate, and are converted into the normal salt by redissolving and precipitating with alcohol. This forms small, lustrous, yellow tablets, which lose their water of crystallisation at 100°. H. G. C.

Mineralogical Chemistry.

Pinakiolite and Trimerite, new Swedish Minerals. By G. FLINK (*Zeit. Kryst. Min.*, **18**, 361—376).—1. *Pinakiolite.*—This mineral was found by the author at Långbanshyttan, in Wermland, with hausmannite in granular limestone. As it always occurs in small, tabular crystals, the name of pinakiolite is suggested, from πινάκιον (small table) and λίθος (stone). The sp. gr. of the mineral is 3·881, and its hardness is 6. It is very brittle, and gave on analysis the following results:—

B_2O_3.	MgO.	Mn_3O_4.	Fe_3O_4.	CaO.	PbO.	SiO_2.	H_2O.	Total.
15·65	28·58	49·39	2·07	1·09	0·76	1·21	0·47	99·22

The formula is $(MgO)_3,B_2O_3,MnO,Mn_2O_3$. Pinakiolite belongs to the rhombic system. It is quite black in colour, and has a strong metallic lustre. In composition it resembles ludwigite.

2. *Trimerite.*—This mineral was found by the author in the Harstigs mine, in Wermland, and is named from τριμερής (divided in three) in reference to the form of the crystals. It occurs in granular limestone, in crystals always surrounded by calcite. Its sp. gr. is 3·474, and its hardness is 6 to 7. On analysis, it yielded:—

SiO_2.	BeO.	MnO.	FeO.	CaO.	MgO.	Total.
39·77	17·08	26·86	3·87	12·44	0·61	100·63

Its formula is $(Mn,Be)SiO_4$. The mineral crystallises apparently in the hexagonal system. Its optical properties, however, prove that it must be regarded as being composed of asymmetric individuals grouped together in a mimetic manner. B. H. B.

Synthesis of Kainite and Tachhydrite. By A. DE SCHULTEN (*Compt. rend.*, **111**, 928—930).—A solution of 500 grams of magnesium chloride, 40 grams of potassium sulphate, and 56 grams of crystallised magnesium sulphate is evaporated on a water-bath. When the solution is sufficiently concentrated, small crystals of kainite separate, and can be freed from magnesium chloride and from carnallite by washing with absolute alcohol. An excess of magnesium sulphate helps to prevent the formation of carnallite, but gives a product containing a slight excess of magnesium. One sample of crystals had the composition—

SO_3.	MgO.	Cl.	K.	H_2O.	Total.
33·30	17·17	14·03	15·09	20·50	100·09

which agrees closely with the formulæ $KCl,MgSO_4,3H_2O$ or $K_2SO_4,MgSO_4,MgCl_2,6H_2O$. Water decomposes the crystals rapidly, magnesium chloride passing into solution, whilst picromerite, $K_2SO_4,MgSO_4,6H_2O$, separates in microscopic crystals. Artificial kainite forms tabular, monoclinic crystals with hexagonal or quadratic contours; sp. gr. 2·120 at 15°, that of the natural mineral being 2·151. Details of the measurements of the crystals are given.

Tachhydrite, $CaCl_2,2MgCl_2,12H_2O$, is obtained in large, but extremely deliquescent crystals, by the evaporation of a solution containing 200 grams of anhydrous calcium chloride and 150 grams of crystallised magnesium chloride. The crystals are rhombohedrons, and their composition agrees closely with that of the mineral; sp. gr. 1·666 at 15°, that of the mineral being 1·671. C. H. B.

Castanite. By L. DARAPSKY (*Jahrb. f. Min.*, 1890; ii, Ref. 267—269).—In a specimen of crystallised iron sulphates, from Sierra Gorda, in Chili, the author thought, at first, that he detected the mineral described by Frenzel as hohmannite (Abstr., 1890, 456). Closer investigation proved, however, that this was a new ferric sulphate, which the author terms castanite. It crystallises in prismatic groups, probably of the monoclinic system. It is of a chestnut-brown colour, with an orange streak and a yellowish-orange powder. It is transparent, has a vitreous lustre, a hardness of 3, and a sp. gr. of 2·18. It is distinctly attacked by water, and is soluble with difficulty in hydrochloric acid. On analysis, it gave the following results:—

SO_3.	Fe_2O_3.	H_2O.	Al_2O_3.	BaO.	Total.
33·80	33·92	30·76	trace	1·15	99·63

Its formula is $Fe_2O_3,2SO_3,8H_2O$. The other known natural ferric sulphates are:—

Amarantite	$Fe_2O_3,2SO_3,7H_2O$.
Hohmannite	$2Fe_2O_3,3SO_3,13H_2O$.
Paposite	$2Fe_2O_3,3SO_3,10H_2O$.

B. H. B.

The Proportion of Molybdenum in Scheelite. By H. TRAUBE (*Jahrb. f. Min.*, Beilage **7**, 232—245).—Scheelite has hitherto been considered to be a calcium tungstate, in which tin oxide, fluorine, chlorine, cupric oxide, the oxides of didymium, cerium, and lanthanum, and traces of magnesium, have at various times been observed as admixtures. On analysing with great care a specimen of scheelite from South-west Africa, the author detected a considerable proportion of molybdenum. Thinking that this metal might occur in scheelite from other localities, the author made a series of analyses, the results being that molybdenum was met with in every case in smaller or larger quantities. The method employed for the quantitative separation of molybdic acid from tungstic acid was essentially that given by H. Rose. The following are the analytical results given by the author :—

	WoO_3.	MoO_3.	CaO.	Total.	Sp. gr.
1*a*	71·08	8·23	20·33	99·64	5·88
1*b*	75·29	3·98	20·34	99·61	6·03
1*c*	76·78	3·69	19·86	100·33	6·01
1*d*	77·84	2·23	19·48	99·55	6·03
1*e*	78·04	1·92	19·57	99·53	6·06
2	77·54	2·03	19·91	99·48	6·07
3*a*	79·94	trace	19·57	99·51	6·12
3*b*	80·17	0·07	19·49	99·83	6·02
4	79·76	trace	19·67	99·43	6·13
5	80·16	trace	19·65	99·81	6·14
6*a*	78·57	1·62	19·37	99·56	6·03
6*b*	79·68	0·76	19·29	99·73	6·04
7	79·97	0·35	19·27	99·59	6·01
8*a*	70·56	8·09	20·05	98·70	5·96
8*b*	71·59	7·63	20·51	99·53	5·96
9	79·77	trace	19·65	99·42	6·09
10	80·29	trace	19·44	99·73	6·01

The localities from which the material was obtained were the following:—1. Zinnwald, Saxony (*a*, reddish-brown crystals; *b*, yellowish-brown, imperfect crystals; *c*, yellow, translucent crystals; *d*, yellow, imperfect crystals; *e*, greyish-white mass); 2. Altenberg; 3. Fürstenberg, Saxony (crystals consisting of white octahedral centre, *a*, and a yellow coating, *b*); 4. Schlackenwald, Bohemia; 5. Guttannen, Switzerland; 6. Traversella (*a*, large, yellow crystals; *b*, translucent, yellow crystals); 7. Carrock Fall, Cumberland; 8. Pot Mine, South-west Africa (specimens contain copper and lime); 9. Mount Ramsay, Tasmania; 10. New Zealand. Besides these, analyses were made of scheelite from Neudorf, in the Harz, and from the Riesengrund, in Bohemia, distinct traces of molybdenum being obtained in each case.

B. H. B.

Manganopectolite. By J. F. WILLIAMS (*Zeit. Kryst. Min.*, **18**, 386—389).—This mineral occurs with thomsonite and other alteration products of elæolite-syenite at Magnet Cove, Arkansas. On the crystals, the planes observed were $0P$, $\infty\bar{P}\infty$, $+2\bar{P}\infty$, $\infty\breve{P}\infty$. The hardness of the mineral is 5 and its sp. gr. is 2·845. Analysis gave the following results :—

SiO_2.	Fe_2O_3.	CaO.	MnO.	Na_2O.	H_2O.	CO_2.	Total.
53·03	0·10	30·28	4·25	8·99	2·43	0·82	99·90

Its formula is $(\frac{9}{10}Ca\frac{1}{10}Mn)_2NaHSi_3O_9$. These results, as well as those of the optical examination, show the close connection between this mineral and pectolite. As this new zeolite differs from pectolite chiefly in its percentage of manganese, the author suggests for it the name of manganopectolite. B. H. B.

Identity of Violan and Anthochroite. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1890, ii, Ref. 270—271).—From the results of analyses of violan and anthochroite, the author concludes that these two minerals are identical, and proposes to include them both under the name of anthochroite. Analyses of violan by E. Schluttig (I), and of anthochroite by the author (II), gave the following results :—

	SiO_2.	Al_2O_3.	CaO.	MgO.	MnO.	FeO.	Na_2O.	K_2O.	Co.Ni.	Total.
I.	51·81	2·59	22·62	14·16	2·58	0·79	5·00	0·25	0·37	100·17
II.	51·60	1·40	23·30	13·50	3·40	—	6·80		—	100·00

B. H. B.

Chrysotile from the Pyrenees. By H. GOGUEL (*Zeit. Kryst. Min.*, **18**, 447; from *Bull. Soc. Chim.*, **11**, 155).—The mineral occurs at Medoux, near Bagnères de Bigorre, in veins a few inches in thickness, in serpentine, which is enclosed in blocks in a limestone breccia. The mineral is apple-green in the interior of the serpentine, and golden-yellow in the vicinity of the surrounding limestone, and whilst the optical characteristics are those of a normal chrysolite, the analysis yielded—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	H_2O.
33·3	5·0	7·5	23·7	12·3	17·5

B. H. B.

Offrétite, a New Mineral. By F. GONNARD (*Compt. rend.*, **111**, 1002—1003).—Offrétite is a zeolite which occurs in very small quantity, associated with christianite and chabasite, in the basalt of Mount Simionse, near Montbrison. It forms small, brilliant, limpid, colourless crystals with a hexagonal aspect, and without any modification of the edges of the base or the faces of the prism. It polarises light feebly; the sign of elongation is positive, and plates perpendicular to the axis show sections analogous to those given by herschelite. Offrétite is brittle, cleaves in a direction normal to the base, and has a vitreous fracture; sp. gr. 2·13. It has the composition—

SiO_2.	Al_2O_3.	CaO.	K_2O.	H_2O.	Total.
52·47	19·06	2·43	7·72	18·90	100·58

which may be represented by the formula $2(K_2,Ca)O,3Al_2O_3,14SiO_2 + 17H_2O$. Before the blow-pipe, it becomes white, and melts to a white enamel without intumescence; with microcosmic salt, it gives a skeleton of silica; heated in a closed tube, it evolves water. Offrétite is attacked with difficulty even by hot acids; when fused with pure calcium carbonate, it yields a very pale brown, homogeneous glass with a slightly greenish fracture. C. H. B.

French Minerals. By A. Lacroix (*Zeit. Kryst. Min.*, **18**, 439—440; from *Bull. Soc. Chim.*, **11**, 70, 148).—*Albite*, from Pouzac (Hauts-Pyrénées), occurs in yellow limestone. The crystals are white and opaque, or transparent, and filled with black pigment irregularly distributed. The black crystals (sp. gr. 2·563) gave, on analysis, the following results:—

SiO_2.	Al_2O_3.	Na_2O.	CaO.	Ignition.	Total.
67·04	20·45	10·57	0·65	1·30	100·01

The author also describes *orthoclase* from Matour (Saône-et-Loire), *rutile* from the slates of the Mont Cenis, and *manganese epidote* from the mica-schist of the Island of St. Groix. B. H. B.

Kryokonite. By E. A. Wülfing (*Jahrb. f. Min.*, Beilage **7**, 152—174).—The material examined by the author was the cosmic dust collected by A. E. Nordenskiöld, in Greenland, in 1883. The author gives a summary of the literature relating to kryokonite. A new analysis of material from which all magnetic particles were removed by means of the magnet gave the following results:—

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Ignition.	Total.
62·08	14·79	4·54	4·65	2·32	1·73	3·52	6·75	100·38

The dust appears to be fairly homogeneous. The author's experiments prove that the kryokonite of 1883 consists for the most part of felspar, quartz, mica, and hornblende. Felspar occurs in greatest quantity; quartz forms some 15 per cent. of the mass, whilst hornblende and mica are present to a less extent. The accessory minerals are pale-pink garnet rich in magnesia, rhombic pyroxene, zircon, and magnetite. In one case, monoclinic pyroxene and sillimanite were observed. The admixed organic matter forms one-twentieth of the powder. It contains nitrogen, and yields, on distillation, ammonia and organic bases. It further contains small quantities of humic acid. Small chondritic masses indicate a meteoric origin for the dust. Metallic iron could not be detected. The cosmic portion is, however, a very small one, and it is possible that a portion of the dust was an air sediment of the detritus of crystalline rocks.

B. H. B.

Organic Chemistry.

Allyl Fluoride. By H. MESLANS (*Compt. rend.*, **111**, 882—883).—Allyl iodide is allowed to fall drop by drop on silver fluoride contained in a copper flask heated to 35° and fitted with a serpentine condenser cooled to 2—3°. The gas is passed through a tube containing silver fluoride heated to 60°, and is collected over mercury.

Allyl fluoride, C_3H_5F, is a colourless gas with an alliaceous odour and a burning taste; sp. gr. at 16° = 2·11 (calc. 2·10). It ignites readily, and burns with a smoky flame which evolves large volumes of hydrogen fluoride. It liquefies at about 1° under normal pressure. Water dissolves 2·5 vols. of the gas at 15°; alcohol dissolves 60 vols. at 16°, and ether more than 100 vols. Induction sparks decompose the gas readily with formation of a large proportion of acetylene and a considerable increase in volume; carbon is deposited round the electrodes and on the walls of the apparatus, and the glass of the latter is strongly attacked. When the gas is heated below dull redness in a glass vessel, there is an abundant deposit of carbon, a small quantity of silicon fluoride is formed, and the residual gas contains a large proportion of methane, but no acetylene. When sodium is heated in the gas, the metal is quickly covered with a thick deposit of carbon, and the gas increases in volume, and contains a considerable quantity of methane. Crystallised silicon behaves practically in the same way as glass, and phosphorus has no action even at its boiling point.

Allyl fluoride is not affected by hot aqueous potash, and is only slowly decomposed by alcoholic potash; lime-water and baryta-water act but slowly on it. Aqueous ammonia does not dissolve the gas, but ammoniacal cuprous chloride absorbs a considerable quantity with formation of a yellowish-white precipitate and separation of a very volatile liquid which seems to be allyl chloride. C. H. B.

Action of Nitriles on Organic Acids. By C. E. COLBY and F. D. DODGE (*Amer. Chem. J.*, **13**, 1—12).—The authors have determined the behaviour of acetonitrile, propionitrile, benzonitrile, and phenylacetonitrile when heated with the common organic acids in sealed tubes, at temperatures between 230° and 280°, to be as follows:—(1.) Fatty nitriles and fatty acids give secondary amides. (2.) Fatty nitriles and aromatic acids exchange their cyanogen and carboxyl groups, giving fatty acids and aromatic nitriles. (3.) Aromatic nitriles and fatty acids give mixed secondary amides. (4.) Aromatic nitriles and aromatic acids, as a rule, give rise to secondary amides, although at high temperatures the nitrile of a higher radicle may be formed.

The secondary amides probably have the unsymmetrical formula $R'\cdot CO\cdot O\cdot RC\vdots NH$, since they are produced by a change analogous to that of the spontaneous conversion of orthocyanobenzoic acid into phthalimide (compare Liebermann, Abstr., 1887, 45).

G. T. M.

Reactions of Potassium Ferricyanide. By PRUD'HOMME (*Chem. Centr.*, 1890, ii, 783—784; from *Mon. Sci.* [4], **4**, ii, 899—902).—*Action of Metals and Metallic Oxides.*—As a rule, metals do not exert any deoxidising action on potassium ferricyanide. With copper, copper potassium ferrocyanide, $K_2CuFeCy_6$, and potassium ferrocyanide are formed. With cupric hydroxide, it becomes oxidised; with lead hydroxide, potassium lead ferrocyanide, potassium ferrocyanide, lead dioxide, and water are formed; lead carbonate reacts similarly.

In addition to the salts obtained by Wyrouboff and Rammelsberg, the author finds that lead nitrate reacts but slowly in the cold with potassium ferricyanide; a greenish precipitate is formed which decolorises indigo at ordinary temperatures.

With potassium chlorate, potassium ferricyanide reacts, as already intimated by Jeanmaire, with formation of ferrocyanide, chloric acid, oxygen, and potassium chloride, but the author considers that all three compounds are formed at the same time, and not in stages. Indigo is decolorised at the ordinary temperature.

With potassium dichromate, potassium ferricyanide does not react; but with the chromate, potassium ferrocyanide and potassium dichromate are formed.

A concentrated solution of nitroprusside is prepared by adding to a solution of 34·5 grams of sodium nitrite in 150 grams of water and 120 grams of a solution of sodium hydrogen sulphite of 37° B. to 82 grams of potassium ferricyanide in 250 grams of water. The mixture is heated until oxygen ceases to be disengaged, and a further 120 grams of the sulphite solution added, when, on cooling the dark red solution, a crystalline salt separates which in boiling water decomposes into Prussian blue and sulphuric acid, and is probably the same compound as that formed by dissolving Prussian blue in concentrated sulphuric acid. A still better yield of nitroprusside is obtained by boiling a solution of 34·5 grams of sodium nitrite, 15 grams of sodium thiosulphate, and 41 grams of potassium ferricyanide in 400 grams of water, and, after cooling, adding 120 grams of sodium hydrogen sulphite solution of 37° B. A brown precipitate also forms, which is soluble in concentrated hydrochloric acid. Sodium polysulphide gives a beautiful dichroic solution with the nitroprusside; in transmitted light, it appears a purple-red; in reflected light, it appears blue. J. W. L.

Constitution of Fulminic Acid. By A. F. HOLLEMAN (*Ber.*, **23**, 3742—3744).—See p. 446.

Behaviour of Ethyl Ether with Sulphuric Acid: Separation of Ethyl Ether from Ethyl Bromide. By L. SCHOLVIEN (*Chem. Centr.*, 1890, ii, 782—783; from *Apoth. Zeit.*, **5**, 607—608).—Owing to the contradictory statements regarding the behaviour of ethyl ether with sulphuric acid to be found in text books, the author was led to determine exactly under what conditions the two react together.

On mixing them much heat is developed, but at ordinary temperatures there is neither at once nor after a time any chemical combination of the two, and dilution with water causes their separation unchanged.

If the mixture is heated at 100° for some time (30 hours), much ethyl hydrogen sulphate is formed, together with a little diethyl sulphate; by heating strongly, sulphurous anhydride, ethylene, and water are formed.

The separation of ethyl ether from ethyl bromide, in which it usually is present when first prepared, may be readily effected by a patented process of Riedel and Co., which consists in slowly adding an equal weight of sulphuric acid to the impure ethyl bromide contained in a reflux apparatus. J. W. L.

Production of Higher Alcohols in Fermentation. By L. Lindet (*Compt. rend.*, **112**, 102—104).—The production of higher alcohols is very slow at first, but increases as fermentation progresses, and continues with still greater rapidity after fermentation proper has ceased. In one case, the quantities of higher alcohols per litre at various times after the commencement of fermentation were as follows:—14 hours, 3·64 c.c.; 20 hours, 4·45 c.c.; 38 hours (fermentation complete), 6·44 c.c.; 24 hours later, 9·2 c.c. It follows that the higher alcohols are not simply products of the normal fermentation of sugar. Their formation seems to take place chiefly under those abnormal conditions of yeast life consequent on the disappearance of the sugar; they may also be produced by some special microorganism which at first is almost inactive in presence of the rapidly developing and vigorous yeast, but becomes active when the work of the yeast is finished. It is clear that the longer the time between fermentation and distillation, the greater the proportion of higher alcohols in the product. C. H. B.

The Pentaglucoses (Pentoses). By W. E. Stone (*Ber.*, **23**, 3791—3798).—It has been shown by Tollens and his pupils, in the course of their researches on this group of sugars, that both arabinose and xylose are readily acted on by strong acids with formation of furfuraldehyde, the quantity of which may be approximately determined by conversion into furfuramide. Further, they have shown that when any quantity of furfuraldehyde is obtained by distilling vegetable products with strong acids, it may be regarded as showing the presence of pentoses or pentose-forming compounds in those products. The author has, therefore, investigated the action of acids on 37 different products, and in the following 29 cases obtained quantities of furfuramide varying from 0·4 per cent. in the first case to 8·16 per cent. in the last:—Clover ensilage, oatmeal, maize and cob meal, orange peel, maize ensilage, white lupine seeds, timothy hay, linseed meal, clover hay, yellow lupine seeds, maize bran, malt sprouts, coats of orange seeds, strawberry pulp, oat straw, water melon seeds, maize straw, Hungarian grass, beet pulp, cotton seed hulls, cowdung, wheat straw, peach gum, gum arabic, gum tragacanth, cherry gum, brewers' grains, maize cobs. The following eight substances did not yield appreciable quantities of furfuraldehyde, but all gave the qualitative reaction with paper soaked in aniline acetate:—Cotton-seed cake, ground maize, sweet potatoes, linseed cake, orange pips, coffee beans, buckwheat, and common beans.

Quantitative estimations have also been made of the reducing power of the pentoses on Fehling's solution. It was found that in solutions containing 1 per cent. or less of arabinose 1·9—2·0 milligrams of copper were precipitated by 1 milligram of arabinose, whilst 1 milligram of xylose under similar conditions precipitates 1·86—1·96 milligrams of copper. Both compounds, therefore, have a stronger reducing action than glucose, which precipitates 1·8—1·9 milligrams of copper.

Numerous attempts were also made to bring about the fermentation of xylose under conditions similar to those which cause the fermentation of the less readily attacked hexoses, such as galactose, but in every case without success. H. G. C.

Pine Tree Honey-dew and Pine Tree Honey. By H. W. Wiley (*Amer. Chem. J.*, **13**, 24—29).—The honey-dew was collected drop by drop from the pine leaves. It contained 54·41 per cent. of water and 45·59 per cent. of solid matters. Calculated as dextrose, it contained 17·44 per cent. of reducing sugar, and after inversion the increase in reducing power was equivalent to 8·16 per cent. of sucrose. The calculated specific rotatory power of the solid, other than dextrose and sucrose, was $[\alpha]_D = 105$, the substance possibly consisting of arabinose or perhaps a mixture of sugars.

Pine tree honey is made by the bees from the pine leaves during the winter. The sample examined differed from the honey-dew in being lævorotatory, even to a greater extent than usually exhibited by honeys. It must consequently be inferred that the bees in gathering the honey exercised an inverting effect on it, or that the sample was not authentic (compare Amthor and Stern, *Zeit. ang. Chem.*, 1889, 575). G. T. M.

Reduction of Fruit Sugar. By E. Fischer (*Ber.*, **23**, 3684—3687).—When an ice-cold solution (10 per cent.) of fruit sugar is reduced with sodium amalgam (2·5 per cent.), a mixture is obtained consisting of 30—40 per cent. of mannitol and 50 per cent. of crude, syrupy sorbitol, which can be separated by crystallisation, and yields 15 per cent. of pure, crystalline sorbitol. The latter crystallises in aggregates of slender, colourless needles; when air-dried, it melts at 55°, and at 75° when dried in a vacuum over sulphuric acid (compare Boussingault, who gives the melting points 60° and 100°, *Ann. Chim. Phys.* [4], **26**, 376). The author points out that on reduction of fruit sugar the carbonyl carbon atom becomes asymmetrical; hence stereoisomerides are probable, and that this is the second reaction resulting in the formation of an asymmetrical carbon atom amongst compounds of the sugar group in which two stereoisomerides which do not combine together are formed. E. C. R.

Synthesis of a New Glucobiose. By E. Fischer (*Ber.*, **23**, 3687—3691).—The author has obtained from glucose a new glucobiose, which from its properties is doubtless constituted like maltose, and is hence called isomaltose. *Isomaltose* is obtained when pure glucose (100 grams) is dissolved in hydrochloric acid (400 grams) of sp. gr. 1·19 at the ordinary temperature, and the mixture allowed to remain for 15 hours at 15°—10°. The product obtained after precipitation with alcohol and ether, is a mixture of grape-sugar, isomaltose, and other substances, from which the isomaltose is separated by means of its osazone. *Isomaltosazone*, which is only obtained at the rate of 2·5 per cent. of the glucose employed, crystallises from water in minute needles, which congregate together in yellow flocks, begins to soften at 140°, and melts between 150°—153°. By rubbing it with strong hydrochloric acid, it is converted into isomaltosone, and this, on hydrolysis with 4 per cent. acid, yields glucose. E. C. R.

A Sugar from the Pectin of Plums. By R. W. Bauer (*J. pr. Chem.* [2], **43**, 112).—The 40 grams of pectin obtained from 20 kilos. of plums in 1885 was heated for four hours with 400 grams of 5 per cent. sulphuric acid, and the still uninverted residue again heated for four hours with 300 grams of the same sulphuric acid; these inversions were mixed together, neutralised with chalk, and the evaporated syrup extracted with 90 per cent. alcohol. After five years, the still uncrystallised liquid was warmed with phenylhydrazine acetate, whereby a yellow phenylglucosazone, optically inactive in water and in alcohol, and melting at 156°, was obtained. Arabinosazone and xylosazone both have this melting point, but behave differently towards polarised light. A. G. B.

Action of Aqueous Ammonia on Isopropyl Iodide and Chloride. By H. Malbot and A. Malbot (*Bull. Soc. Chim.* [3], **4**, 340, 632, 634).—Isopropyl iodide and saturated aqueous ammonia are placed in sealed tubes; at the ordinary temperature, after some months, the reaction is complete, monisopropylamine iodide alone being formed.

When a similar mixture is heated in sealed tubes at 100°, the reaction is complete after four days; some propylene is formed, but the monisopropylamine iodide contains but traces of diisopropylamine iodide.

When isopropyl chloride is heated with strong aqueous ammonia in sealed tubes at 140°, much propylene is formed, and the resulting liquid separates into two layers. The supernatant fluid contains monisopropylamine, diisopropylamine, and some isopropyl chloride, whilst the aqueous layer contains monisopropylamine and diisopropylamine chlorides, the isopropyl chloride differing thus from the isopropyl iodide in furnishing free amines, and in the reaction not being complete. T. G. N.

Preparation of Lecithin from Plant Seeds. By E. Schulze and A. Likiernik (*Ber.*, **24**, 71—74).—Lecithin is always considered as being widely distributed in the vegetable kingdom, from the fact that the ethereal extract of many parts of plants contains phosphorus, and on hydrolysis yields choline and other decomposition products of lecithin. Hitherto, however, it has not been isolated from plants, the difficulty being that the ethereal extract contains glycerides, waxes, cholesterin, &c., which are not readily separated. It was observed some time since (Abstr., 1889, 645) that finely powdered plant seeds only yield a portion of their lecithin on extraction with ether, the remainder being then obtained from the residue by treatment with hot alcohol. It is probable that the second portion of lecithin forms, with another substance present, an unstable compound which is decomposed by the hot alcohol. If the alcoholic solution be evaporated and treated with ether, the lecithin is taken up by the latter, and impurities may be removed by shaking the ethereal solution with water; an emulsion is first obtained, but on addition of sodium chloride this separates into two layers.

Lecithin solutions were obtained in this manner from vetch and lupine seeds; they were evaporated by gently warming, and the residue treated with absolute alcohol at 50°. The solution is cooled in a freezing mixture, and the precipitate obtained is washed with cold alcohol and dried over sulphuric acid. The product has a yellowish colour, and shows all the properties of lecithin. Its alcoholic ethereal solution gave with alcoholic platinic chloride a yellowish-white precipitate, and on hydrolysis gave the same products as animal lecithin, namely choline, glycerol, phosphoric acid, fatty acids, and also oleic acids, showing that the product is a mixture of several lecithins.

In the quantitative estimation of the fatty constituents of seeds, a correction must be made for the quantity of lecithin taken up by the ether, which is readily done by estimating the phosphorus in the extract, and subtracting the corresponding quantity of lecithin.

H. G. C.

Ethylene Bases. By A. W. v. Hofmann (*Ber.*, **23**, 3711—3718). —The author has shown in a former paper on the preparation of ethylene bases (this vol., p. 169), that on hydrolysis of the product formed by the action of ammonia on bromethylene, basic oils are obtained, and these on distillation show a continuously rising boiling point, which exceeds finally the limit of the mercurial thermometer. These oils contain diethylenediamine and higher members of the ethylene bases. The fraction from 117° to 121° yields ethylenediamine on redistillation; the fraction from 200° to 225°, on the addition of hydrogen chloride, gives a crystalline salt, which consists for the most part of diethylenetriamine hydrochloride (*Proc. Roy. Soc.*, **11**, 420). The fraction from 250° to 300° gives, on addition of hydrogen bromide, triethylenetetramine hydrobromide, $C_6H_{18}N_4,4HBr$. The same compound, together with diethylenediamine and other products, is also formed by digesting ethylene chloride (1 mol.) with ethylenediamine (3 mols.) on the water-bath, and subsequent treatment of the product with potash and fractionation of the oil so obtained. The fraction from 200° to 300° is converted into the hydrochloride, decomposed with silver hydroxide, and saturated with hydrogen bromide.

Triethylenetetramine, obtained from the hydrobromide by hydrolysis with potash, boils at 266—267°, is a colourless, viscous liquid, but becomes limpid on gentle warming, and dissolves in water with development of much heat; the solution gives a strongly alkaline reaction, and absorbs carbonic anhydride with avidity. Sp. gr. = 0·9817 at 15°. At −18°, it solidifies to a radiated crystalline mass, which melts at +12°. The *hydrobromide*, $C_6H_{18}N_4,4HBr$, crystallises from dilute alcohol with 1 mol. H_2O in hemimorphic prisms belonging to the rhombic system, $a : b : c = 0·5654 : 1 : 0·5014$. It is extremely soluble in water, slightly soluble in alcohol, and must be crystallised from a solution containing an excess of hydrogen bromide. A hydrobromide of the formula $C_6H_{18}N_4,3HBr$ crystallises from neutral solutions. The hydrochloride, $C_6H_{18}N_4,4HCl$, resembles the hydrobromide, and is best purified by solution in water and precipitation with alcohol. The *platinochloride*, $C_6H_{18}N_4,2H_2PtCl_6$, is obtained in thin plates, and dissolves sparingly in water. The *aurochloride*, $C_6H_{18}N_4,4HAuCl_4$, obtained in concentrated solutions, crystallises from hot water in beautiful, glistening plates. A second salt of the formula $C_6H_{18}N_4,4HCl,8AuCl_3$ is obtained on boiling a dilute solution of the hydrochloride with excess of gold chloride, and is insoluble in water. A corresponding platinum salt could not be obtained.

Other salts of the tetramine were prepared, but not examined in detail; they are all, except the oxalate, easily soluble in water, and are precipitated from their solutions on the addition of alcohol. Methyl iodide acts on the tetramine with great violence. The *benzoyl compound*, $C_6H_{14}N_4Bz_4$, is easily prepared in alkaline solution, melts at 228—229°, crystallises from amyl alcohol in small needles, and is sparingly soluble in ethyl alcohol. E. C. R.

Piperazine. By W. Majert and A. Schmidt (*Ber.*, **23**, 3718—3723).—The authors come to the conclusion that Hofmann's diethylenediamine, Schreiner's spermine, Ladenburg's ethylenimine, and piperazine are identical.

Ladenburg gives the melting point of the base as 159—163°. Piperazine melts at 104—107°; it, however, eagerly absorbs carbonic anhydride with formation of the carbonate, which melts at 162—165°, and Ladenburg was no doubt dealing with the carbonate. Piperazine forms with uric acid the neutral and easily soluble salt of the formula $C_4N_2H_{10},C_5N_4H_4O_3$, which dissolves in 50 parts of water at 17°. The base has neither caustic nor toxic properties. E. C. R.

Action of Heat on the Hydrochlorides of Ethylene Bases. By A. W. v. Hofmann (*Ber.*, **23**, 3723—3726).—Diethylenetriamine hydrochloride melts when cautiously heated; if, however, the temperature be raised, carbonisation takes place, and empyreumatic vapours and a crystalline sublimate are obtained. Diethylenediamine is obtained by extraction of the carbonised mass with water, and is recognised by converting it into the benzoyl compound, which melts at 191°. Triethylenetetramine hydrochloride, when treated in the same way, also yields diethylenediamine. Ethylenediamine hydrochloride yields diethylenediamine, but not with the same ease as the above compounds. Diethylenediamine hydrochloride gives on distillation the free base, but the greater part is decomposed. Amongst the products of the action of ammonia on ethylene chloride, bases of high boiling point (above 300°) are formed, which have not been examined; they give, however, on distillation, diethylenediamine. The author prefers the name diethylenediamine to piperazine (*Ber.*, **23**, 3718—3723). E. C. R.

Diethylenediimine (Piperazine). By A. LADENBURG (*Ber.*, **23**, 3740—3741).—The product obtained by the distillation of ethylenediamine hydrochloride is probably diethylenediamine, and not diethylenediimine as previously stated, since it yields a benzoyl derivative which melts at 191°, and the free diamine has been shown by Hofmann to be capable of crystallisation (compare this vol., p. 169). J. B. T.

Guanamines. By C. HAAF (*J. pr. Chem.* [2], **43**, 75—85).—*Propionoguanamine* is prepared by heating guanidine propionate (obtained by decomposing guanidine carbonate with propionic acid) in a flask on the sand-bath at 220—230° for some hours, dissolving the melt in water, filtering hot, and adding strong soda solution, which precipitates the base. It is best purified by conversion into the hydrochloride and subsequent decomposition with sodium hydroxide. It crystallises from water in anhydrous, quadratic pyramids; in a capillary tube, it blackens at 300° without melting; it dissolves freely in hot water and in alcohol. The *hydrochloride* is anhydrous.

Œnanthoguanamine is similarly obtained, but the white precipitate at first formed on addition of strong soda solution rapidly collects as an oily layer. It crystallises in tables and prisms, melts in a capillary tube at 130°, and is sparingly soluble in water, but freely in alcohol.

Attempts to prepare caprylоguanamine and capriguanamine by this method have failed.

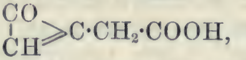
The guanamines of the volatile fatty acids afford excellent means for the identification of these acids; the first seven of the series are now known (see also this Journal, 1874, 1089; 1875, 754; 1876, ii, 187, 190); and in this paper the author gives figures of the crystalline forms of these seven. A. G. B.

Action of Hydroxylamine on Acetoacetaldehyde. By L. CLAISEN and E. HORI (*Ber.*, **24**, 139—140).—A compound of the formula $C_8H_{13}N_3O_3$ is obtained when sodium acetoacetaldehyde (40 grams) dissolved in water (60 c.c.) at 0° is mixed with hydroxylamine hydrochloride (26 grams) dissolved in water (20 c.c.), and the pale-yellow solution allowed to crystallise over sulphuric acid. It crystallises from hot alcohol in small, white needles, melts at 174°, and is sparingly soluble in water, ether, benzene, chloroform, and light petroleum. The oxime, cyanacetone, and methylisoxazole, which are probable products in this reaction (see p. 451), have not yet been obtained. E. C. R.

Glyoxylpropionic Acid and its Derivatives. By L. WOLFF (*Annalen*, **260**, 79—136).—When levulinic acid is treated with bromine, it is converted into a dibromo-acid identical with that obtained by brominating β-bromolevulinic acid (Abstr., 1885, 1123).

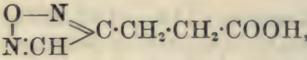
This compound melts at 114—115°, and is isomeric, but not identical, with the $\alpha\beta$-dibromo-acid, which is formed by the addition of bromine to acetylacrylic acid; it must, therefore, have the constitution represented by one of the following formulæ:—

$$COMe\cdot CBr_2\cdot CH_2\cdot COOH \text{ and } CH_2Br\cdot CO\cdot CHBr\cdot CH_2\cdot COOH.$$

When it is boiled with water (10 parts) for 5 to 6 hours, it is completely decomposed, yielding, as principal product, an acid which is very probably glyoxylpropionic acid, and hydrogen bromide, together with small quantities of diacetyl (m. p. 87—88°) and carbonic anhydride. This decomposition can only be explained by assuming that the dibromolevulinic acid is first converted into a kind of trimethylene derivative of the constitution  $\left.\begin{matrix}CO\\ |\\ CH\end{matrix}\right>C\cdot CH_2\cdot COOH$, by elimination of 2 mols. of hydrogen bromide, and that this intermediate product then combines with water in two ways to form both glyoxylpropionic acid and diacetylcarboxylic acid, the last-named compound being decomposed into diacetyl and carbonic anhydride.

Glyoxylpropionic acid, $COH\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$, can be isolated from the brown aqueous solution obtained by the decomposition of dibromolevulinic acid in the following manner:—The diacetyl is separated by distillation, the hydrobromic acid in solution precipitated with silver carbonate, the filtrate treated with hydrogen sulphide, filtered, and evaporated; the acid is then obtained as a brown oil, which shows no signs of crystallising, but gradually changes into a resinous mass. It is readily soluble in water and alcohol, but only sparingly in the other ordinary solvents; it reduces Fehling's solution and ammoniacal silver nitrate, and it precipitates mercurous chloride from a solution of the mercuric salt. The barium, calcium, and zinc salts are readily soluble in water, and are obtained as dark, amorphous residues on evaporating their solutions. When the acid is oxidised with potassium permanganate in the cold, it is converted into succinic acid and carbonic anhydride.

$\gamma\delta$-Diisonitrosovaleric acid, $NOH:CH\cdot C(NOH)\cdot CH_2\cdot CH_2\cdot COOH$, is formed when glyoxylpropionic acid is treated with hydroxylamine at the ordinary temperature. It crystallises from hot water in well-defined colourless plates, melts at 136°, and is very readily soluble in alcohol and hot water, but less readily in ether and cold water, and only sparingly in chloroform and carbon bisulphide; it dissolves in boiling acetic anhydride, yielding a deep-red solution, and, in its aqueous solution, ferric chloride produces a cherry-red coloration, which changes to yellow on the addition of hydrochloric acid. The barium salt, $(C_5H_7N_2O_4)_2Ba + 3H_2O$, prepared by saturating an aqueous solution of the acid with barium carbonate, crystallises from hot water, in which it is readily soluble, in slender needles, and loses the whole of its water at 110°; in its aqueous solution, ferric chloride produces a brownish-red precipitate which is soluble in excess, yielding a red solution. On oxidation with potassium permanganate in the cold, diisonitrosovaleric acid yields succinic acid, hydrocyanic acid, and nitric acid.

Furazanpropionic acid,  $\begin{matrix}O—N\\ | \\ N{:}CH\end{matrix}\!\!>C{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is produced, together with small quantities of a bluish-black substance, described below, and resinous products, when finely-divided diisonitrosovaleric acid is dissolved in concentrated sulphuric acid (4 parts), the temperature being kept below 70°, the solution then heated for 20 minutes at 100°, and finally poured into cold water (3 vols.); the product is extracted with ether, and recrystallised from hot water with the addition of animal charcoal. It crystallises in lustrous plates, sinters together at about 84°, melts at 86°, and is readily soluble in ether, alcohol, chloroform, and hot water, but rather sparingly in cold water, carbon bisulphide, and light petroleum; it is not volatile with steam. Molecular weight determinations by Raoult's method in glacial acetic acid solution gave results in accordance with the molecular formula $C_5H_6N_2O_3$. The *calcium* salt, $(C_5H_5N_2O_3)_2Ca + 2H_2O$, crystallises from cold water, in which it is readily soluble, in lustrous needles, melts at 100°, and decomposes at 110° without becoming perfectly anhydrous. The *silver* salt crystallises from boiling water in needles, and explodes when heated.

Furazanpropionic acid is very stable, except towards alkalis, and can be heated with concentrated sulphuric acid or nitric acid at 100°, or with concentrated hydrochloric acid at 130°, without any appreciable decomposition taking place; hydroxylamine has no action on it in cold aqueous solution, but on heating at 50—60°, it undergoes intramolecular change into cyanonitrosobutyric acid, which is then converted into the amidoxime described below. It does not combine with bromine in chloroform solution at the ordinary temperature, and tin and hydrochloric acid have no action on it, even at moderately high temperatures. The *anhydride*, $(C_5H_5N_2O_2)_2O$, is formed when furazanpropionic acid is heated with acetic anhydride; it crystallises from chloroform in colourless plates, melts at 67°, and is readily soluble in hot benzene and chloroform, but rather sparingly in water, ether, alcohol, and carbon bisulphide. The freshly prepared aqueous solution of the anhydride has a neutral reaction, but soon becomes acid; when boiled with water or treated with cold sodium carbonate, the anhydride is completely reconverted into furazanpropionic acid.

Cyanonitrosobutyric acid, $NOH{:}C(CN){\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is quickly formed, with slight development of heat, when furazanpropionic acid is treated with excess of soda or ammonia at the ordinary temperature; on acidifying and extracting with ether, the cyano-derivative is obtained as a colourless oil which gradually solidifies. It separates from a mixture of benzene and ether in large, lustrous prisms containing benzene, which escapes on exposure to the air, the crystalline powder then melting at 87°, although it sinters together at 85°. It is not acted on by bromine at the ordinary temperature, and, in its aqueous solution, ferric chloride produces a yellowish-red coloration which disappears on the addition of hydrochloric acid. The *calcium* salt, $(C_5H_5N_2O_3)_2Ca + 2H_2O$, crystallises from hot water in microscopic needles, does not lose its water at 110°, and begins to decompose at

120°. The *silver* salt is a colourless, flocculent compound which melts and turns black when boiled with water.

When furazanpropionic acid is heated at 100° with aniline for several hours, it is partially converted into a compound which crystallises from boiling alcohol in needles, and is insoluble in water and alkalis. This substance, which is very probably the anilide of the acid, melts at 137° without any appreciable decomposition, but when heated at its melting point for some minutes, it solidifies again, having been converted into another crystalline substance which melts at about 184° with decomposition; the latter substance is also produced in very small quantities when furazanpropionic acid is boiled with aniline.

Cyanonitrosobutyric acid gives a very characteristic reaction with concentrated sulphuric acid, and also, but not so well, with concentrated hydrochloric acid; when warmed at about 60° for 1 to 2 minutes with a few drops of the concentrated acid, it yields a yellow solution which, on the addition of a small quantity of water, turns blue at the surface of contact of the two liquids; on agitating, a clear, cherry-red solution is obtained, but if the addition of water is continued, the colour finally changes to blue, and a substance is precipitated in bluish-black needles which dissolve in alkalis and ammonia with a deep-blue coloration, the solution turning red on boiling or on adding a mineral acid.

The *amidoxime*, $NH_2 \cdot C(NOH) \cdot C(NOH) \cdot CH_2 \cdot CH_2 \cdot COOH$, is precipitated in slender needles when a concentrated aqueous solution of sodium nitrosocyanobutyrate is digested with hydroxylamine (1 mol.) at about 50° for some hours, and then acidified with acetic acid; it melts at 158° with decomposition, and is only sparingly soluble in water, alcohol, ether, and chloroform, but readily in dilute hydrochloric acid and sodium carbonate. Its aqueous solution gives, with ferric chloride, a red coloration, and with copper acetate, a dirty-green precipitate which is only sparingly soluble in water; when the amidoxime is boiled with water, it is converted into a crystalline compound which is insoluble in hydrochloric acid. It dissolves in boiling dilute hydrochloric acid, yielding a red solution, which turns blue on the addition of alkalis; these colour reactions are due to the formation of a dark-blue compound which is identical with that produced by the action of concentrated sulphuric acid on nitrosocyanobutyric acid, and also with the dark bye-product obtained in the preparation of furazanpropionic acid.

α-Nitrosoglutaric acid, $COOH \cdot C(NOH) \cdot CH_2 \cdot CH_2 \cdot COOH$, is obtained when cyanonitrosobutyric acid is boiled with potash or barium hydroxide, and when furazanpropionic acid (1 part) is heated with potassium hydroxide (2 parts) and water (6 parts) until the evolution of ammonia is at an end. It crystallises from warm water in ill-defined, colourless prisms, melts at 152° with evolution of carbonic anhydride, and is readily soluble in warm water, but only moderately easily in ether, chloroform, benzene, and cold water; it is decomposed by boiling water with liberation of carbonic anhydride, and, in its aqueous solution, ferric chloride produces a reddish-brown coloration. The normal salts of the alkalis are readily soluble in water, but those of the alkaline earths and the heavy metals are only sparingly soluble; the *potassium* salt is crystalline. The *barium* salt, $C_5H_5NO_5Ba + 1\frac{1}{2}H_2O$, crystallises in lustrous needles, loses about $\frac{1}{2}$ mol. H_2O at 100°, and gradually decomposes at a higher temperature. The *calcium* salt crystallises in broad needles or plates; the *silver* salt is amorphous, and explodes when heated.

Succinamic acid, $C_4H_7NO_3$, is formed when nitrosoglutaric acid is warmed with acetic anhydride until the evolution of carbonic anhydride is at an end; on evaporating the red solution over calcium oxide, there remains a thick syrup, probably acetylsuccinamic acid, from which, on the addition of a little water, succinamic acid is deposited in crystals. It separates from warm water in colourless needles, melts at 157° (not above 300°, as stated by Teuchert, *Annalen*, **134**, 146), and is moderately easily soluble in cold water, but only sparingly in ether, alcohol, chloroform, and benzene; when boiled with water, it is gradually converted into ammonium succinate.

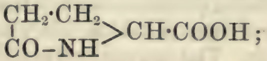
Inactive *glutamic acid* (*amidoglutaric acid*),

$$COOH{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

is obtained when concentrated hydrochloric acid is poured over finely-divided nitrosoglutaric acid and a slight excess of the theoretical quantity of tin added in small portions at a time; the clear, yellow solution is treated with hydrogen sulphide to precipitate the tin, and the filtrate evaporated, when glutamic acid hydrochloride remains as a syrup which gradually solidifies. This salt crystallises from hot hydrochloric acid in needles, melts at about 193° with decomposition, and is very readily soluble in water, to which it imparts an acid reaction; it has all the properties of the hydrochloride of the glutamic acid obtained from albuminoïds, and described by Hlasiwetz and Habermann (*Annalen*, **169**, 157), but unlike the latter, which is dextro-rotatory, it is optically inactive. The two salts are nevertheless identical crystallographically, and form long, colourless plates, $a : b : c = 0{\cdot}8873 : 1 : 0{\cdot}3865$, belonging to the rhombic system. Inactive glutamic acid, prepared by decomposing the hydrochloride with silver carbonate, crystallises from hot water in small, rhombic plates, $a : b : c = 0{\cdot}7454 : 1 : 1{\cdot}2367$, melts at 198° with decomposition (see below), and is readily soluble in boiling water, but only sparingly (1 in 66·7 parts) in water at 20°, and in alcohol, ether, carbon bisulphide, and light petroleum. It differs from the active acid in crystalline form; in its aqueous solution, ferric chloride produces a red coloration. The *copper* salt,

$$C_5H_7NO_4Cu + 2\tfrac{1}{2}H_2O,$$

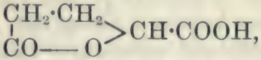
is obtained in blue needles when the acid is boiled with copper carbonate and the deep-blue solution allowed to cool; it loses the whole of its water at 135°, and is not soluble in less than 1000 parts of boiling water, whereas the copper salt of the active acid is soluble in about 400 parts. When the acid is heated at its melting point, it is decomposed into pyrrolidonecarboxylic acid,



$$\left.\begin{array}{l}CH_2{\cdot}CH_2\\ |\\ CO{-}NH\end{array}\right\rangle CH{\cdot}COOH;$$

this compound melts at 182—183°, and is identical with the pyroglutamic acid obtained by Haitinger (*Monatsh.*, **3**, 228) by heating active glutamic acid, and also with the glutimic acid prepared by Schützenberger (*Ann. Chim. Phys.* [5], **16**, 372) by decomposing albumin with barium hydroxide at 180°.

Zinc hydroxyglutarate, $C_5H_6O_5Zn + 3H_2O$, is obtained in crystals when glutamic acid hydrochloride (1 part) is dissolved in ice-cold, very dilute hydrochloric acid, an aqueous solution of potassium nitrite (1 part) added to the solution in the course of a few hours, the mixture kept at the ordinary temperature until gas ceases to be evolved, then diluted, boiled with excess of zinc carbonate, filtered, and evaporated. It crystallises from boiling water in slender needles, and is decomposed by hydrogen sulphide in aqueous solution, yielding γ-hydroxyglutaric acid. Careful experiments showed that this acid is stable in a crystalline condition, but it cannot be isolated; on evaporating its solution at 100°, there remains a thick syrup which gradually solidifies over sulphuric acid to a mass of slender, hygroscopic crystals of butyrolactone-γ-carboxylic acid, $C_5H_6O_4$. The γ-hydroxyglutaric acid (m. p. 72—73°) described by Markovnikoff (*Annalen*, **182**, 347), and also by Ritthausen (*J. pr. Chem.*, **99**, 461) and Dittmar (*ibid.* [2], **5**, 338), as a thick syrup, is doubtless a mixture of the γ-hydroxy-acid and butyrolactone-γ-carboxylic acid.

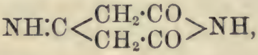
Butyrolactone-γ-carboxylic acid,  $\left.\begin{matrix}CH_2{\cdot}CH_2\\ \vert\\ CO\text{——}O\end{matrix}\right>CH{\cdot}COOH$, melts at 49—50°, and is very readily soluble in water and alcohol, but only sparingly in ether, chloroform, benzene, and carbon bisulphide; when the lactone is treated with cold water, a solution containing 18 per cent. of the hydroxy-acid is obtained, but, on boiling, the quantity of this acid produced amounts to 47 per cent. A *salt* of the composition $(C_5H_5O_4)_2Ca + 2H_2O$ is obtained in crystals when a freshly-prepared aqueous solution of the lactone-acid is neutralised with calcium carbonate in the cold, quickly filtered, and evaporated over sulphuric acid. It is very readily soluble in water, to which it imparts a slight acid reaction; when dried, it loses 2 mols. H_2O. The *zinc* salt, $(C_5H_5O_4)_2Zn + 2H_2O$, prepared in like manner, is amorphous, and very readily soluble in water; it melts at 100°, loses the whole of its water at 100—115°, and, in aqueous solution, is slowly converted into the neutral salt of hydroxyglutaric acid. *Barium butyrolactonecarboxylate*, $(C_5H_5O_4)_2Ba$, is obtained as a colourless, vitreous mass when a concentrated solution of the lactone-acid is treated with excess of barium carbonate at the ordinary temperature, and the filtrate evaporated under reduced pressure; it is readily soluble in water, to which it imparts a slight acid reaction, but is reprecipitated on adding alcohol. The *silver* salt, $C_5H_6O_5Ag_2$, is precipitated, but only in very small quantities, when a concentrated solution of any one of the three salts just described is mixed with silver nitrate, and on boiling the mother liquors, a further separation of the salt takes place; it crystallises from boiling water in colourless needles.

F. S. K.

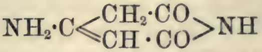
Action of Ammonia, Isobutylamine, and Aniline on Ethyl Acetonedicarboxylate. By W. O. Emery (*Ber.*, **23**, 3761—3765).—By the action of aqueous ammonia on ethyl acetonedicarboxylate, v. Pechmann and Stokes (Abstr., 1885, 1202; 1887, 155) obtained the ethyl salt of β-hydroxyamidoglutamic acid,

$$COOEt\cdot CH_2\cdot C(OH)(NH_2)\cdot CH_2\cdot CONH_2,$$

which undergoes condensation forming the glutazine,



$$NH{:}C<\genfrac{}{}{0pt}{}{CH_2\cdot CO}{CH_2\cdot CO}>NH,$$

or  $NH_2\cdot C<\genfrac{}{}{0pt}{}{CH_2\cdot CO}{CH\cdot CO}>NH$ (*Annalen*, **260**, 160). If the ethyl salt be allowed to remain in the cold with alcoholic ammonia, a different reaction takes place, *ethyl-β-amidoglutaconate*,

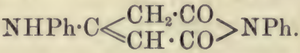
$$COOEt\cdot CH{:}C(NH_2)\cdot CH_2\cdot COOEt,$$

being formed. This is a thick, pale-yellow oil, which boils at 157—158° under 12—13 mm. pressure, and has a sp. gr. of 1·11169 at 20°/4°.

Isobutylamine acts even more readily than ammonia, with formation of *ethyl-β-isobutylamidoglutaconate*,

$$COOEt\cdot CH{:}C(NH\cdot C_4H_9)\cdot CH_2\cdot COOEt,$$

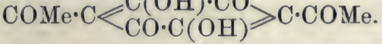
which is also a slightly yellow oil boiling at 181—182° under 17 mm. pressure, and having a sp. gr. of 1·02725 at 20°/4°. Aniline acts in rather a different manner, 1 mol. of water and 2 mols. of alcohol being eliminated. The product is sparingly soluble in alcohol, and crystallises from the solution in slightly yellow plates which melt at 275° with decomposition, and have the composition $C_{17}H_{14}N_2O_2$. It is probably a glutazine derivative of the constitution



$$NHPh\cdot C<\genfrac{}{}{0pt}{}{CH_2\cdot CO}{CH\cdot CO}>NPh.$$

The *oxime* of acetonedicarboxylic acid, $HO\cdot N{:}C(CH_2\cdot COOH)_2$, already shortly mentioned by Pechmann and Wehsarg (Abstr., 1887, 28), is readily prepared by allowing aqueous solutions of the acid and of hydroxylamine to remain together for 24 hours. It is extracted by agitation with ether, and separates on the evaporation of the latter in large, transparent crystals melting at 53—54°. After drying in the exsiccator, a product remains which melts at 89°, and has the composition $C_5H_5NO_4$, and therefore consists of the anhydride. The *silver* salt has the composition $C_5H_5NO_5\cdot Ag_2$, and explodes on heating.

H. G. C.

Coloured Compounds derived from Ethyl Acetonoxalate. By L. Claisen (*Ber.*, **24**, 128—130).—When the colourless sodium salt of ethyl acetonoxalate is heated with glacial acetic acid, the solution becomes of an intense reddish-violet colour (Abstr., 1888, 676). This is due to the formation of characteristically coloured metallic derivatives of the composition $C_5H_3O_3M'$, derived from the substance $C_5H_4O_3$, which contains 1 mol. of water less than acetonoxalic acid, $COMe\cdot CH_2\cdot CO\cdot COOH - H_2O = C_5H_4O_3$. These salts are best prepared by allowing acetonoxalic acid to stand at the ordinary temperature with anhydrous sodium or potassium acetate and acetic anhydride. The alkali salt is formed with the production of an intense violet colour. By adding barium chloride, silver nitrate, &c., to the alkaline derivatives, other metallic derivatives are obtained, which are mostly well crystallised. The potassium and sodium salts are easily soluble in water; the barium, strontium, calcium, and silver salts are sparingly soluble. In aqueous solution they are dark reddish-violet, in solid condition deep bluish-violet, and in compact crystals quite black. These compounds are in some degree like the phthaleïns; excess of alkali turns them bright-yellow; the addition of mineral acids restores the colour, which is again weakened by excess of acid. They are decolorised by sulphurous acid. The author believes the compound to be a diacetylated dihydroxyquinone of the formula  $COMe\cdot C\Big<{C(OH)\cdot CO \atop CO\cdot C(OH)}\Big>C\cdot COMe$.

Ethyl oxalacetate on similar treatment gives blue salts, which, however, are less stable than the above. E. C. R.

Ethyl β-Acetyltricarballylate. By W. O. Emery (*Ber.*, **23**, 3755—3756).—In the preparation of ethyl acetosuccinate from ethyl acetoacetate and ethyl bromacetate on the large scale, considerable quantities of *ethyl β-acetyltricarballylate* are formed, and may be readily separated by fractionating the product under reduced pressure. It boils at 190° under 16 mm. pressure, and has a sp. gr. of 1·12141 at 20°/4°. The compound has previously been obtained in an impure condition by Michle (Abstr., 1878, 490); it combines with phenylhydrazine at the temperature of the water-bath, forming the *hydrazone*, $C_{20}H_{28}N_2O_6$, which, after recrystallisation first from carbon bisulphide and then from ethyl acetate, forms small prisms melting at 100—101°. H. G. C.

A New Synthesis of Tricarballylic Acid and of Certain Ethereal Salts. By W. O. Emery (*Ber.*, **23**, 3756—3761).—The ethyl salt of chlorosuccinic acid readily acts on the sodium compounds of ethyl acetoacetate and of ethyl malonate, with formation of derivatives of tricarballylic acid. Ethyl chlorosuccinate is prepared by saturating an alcoholic solution of the acid with hydrogen chloride; it boils at 122° under 15 mm. pressure, and has a sp. gr. of 1·14557 at 20°/4°. When it is added to an alcoholic solution of ethyl sodacetoacetate, separation of sodium chloride takes place almost immediately, and the reaction is complete in a few minutes. The product is a thick oil, which distils at 175° under 9 mm. pressure, has a sp. gr. of 1·12577 at 20°/4°, and the composition $C_{14}H_{22}O_7$. From its mode of preparation, it must be *ethyl α-acetyltricarballylate*,

$$COOEt\cdot CH_2\cdot CH(COOEt)\cdot CHAc(COOEt).$$

It unites with phenylhydrazine, forming an oily compound, which appears to be *ethyl* 1-*phenyl*-3-*methylpyrazolone*-4-*succinate*, $C_{18}H_{22}N_2O_5$. On hydrolysis, it yields the corresponding acid $C_{14}H_{14}N_2O_5$, which crystallises from water containing sulphuric acid in nodules having a reddish lustre, and melting at 210—212°. Ethyl α-acetyltricarballylate also reacts with alcoholic ammonia, with formation of a well crystallised compound, which is being further investigated.

By the action of ethyl chlorosuccinate on ethyl sodiomalonate, the ethyl salt of *propanetetracarboxylic acid*,

$$COOEt{\cdot}CH_2{\cdot}CH(COOEt){\cdot}CH(COOEt)_2,$$

is obtained. It is an oil which distils at 203—204° under 18 mm. pressure, has a sp. gr. of 1·11841 at 20°/4°, and cannot be distilled under atmospheric pressure without decomposition. It forms a sodium compound, and also combines with chlorine and bromine forming a monochloro- and monobromo-substitution product; by the action of alcoholic potash, it is converted into tricarballylic acid.

Ethyl butanepentacarboxylate,

$$COOEt{\cdot}CH_2{\cdot}CH(COOEt){\cdot}C(COOEt)_2{\cdot}CH_2{\cdot}COOEt,$$

is prepared by acting on the sodium compound of ethyl ethenyltricarboxylate with ethyl chlorosuccinate, and forms a thick, colourless oil, which boils at 216—218° under 16 mm. pressure, and has a sp. gr. of 1·14088 at 20°/4°. H. G. C.

Synthesis of Aconitic Acid. By L. Claisen and E. Hori (*Ber.*, **24**, 120—127).—Ethyl acetate and ethyl oxalate combine in the presence of sodium ethoxide to form ethyl oxalacetate,

$$COOEt{\cdot}CH_2{\cdot}CO{\cdot}COOEt,$$

and this, on remaining with a concentrated solution of potassium acetate, dissolves after a time with the formation of the potassium salt of a monobasic acid of the composition $C_{14}H_{18}O_9$, which was identified as the triethyl salt of aconitoxalic acid. It is best prepared as follows:—Ethyl oxalacetate (37 grams) is mixed with a solution of potassium acetate (20 grams) in 20 c.c. of water, with constant shaking; after some time the mixture becomes clear and slightly warm, and, in consequence of the formation of bye-products, is blue to bluish-green. On acidifying with hydrochloric or sulphuric acid, the product is precipitated as an oil, and can be extracted with ether. It is a colourless liquid of the consistence of glycerol, easily soluble in alcohol and ether, sparingly in water; the alcoholic solution gives an intense red coloration with ferric chloride. The *barium salt*, $(C_{14}H_{17}O_9)_2Ba + 2H_2O$, obtained as a white precipitate on adding barium chloride to a solution of the potassium salt, is very sparingly soluble in water, and crystallises in slender, felted needles which lose their water of crystallisation at 100°, or on remaining over sulphuric acid in a vacuum. The *lead salt*, $(C_{14}H_{17}O_9)_2Pb$, is more insoluble than the barium salt, and is obtained as a crystalline precipitate on adding lead nitrate to the boiling solution of the barium salt. It is somewhat easily soluble in hot alcohol, and, on the addition of water, crystallises in beautiful, short needles.

The conversion of the above acid into aconitic acid is rather a difficult operation, as excess of alkali produces a partial decomposition into acetic and oxalic acids. It is best carried out as follows:—The acid (1 mol.) dissolved in alcohol is mixed with 3 per cent. alcoholic potash (6 mols.), and heated for three hours on the water-bath; one-third of the alcohol is then distilled off, and the product dissolved in water and heated until the solution, on acidification with acetic acid, no longer turns red with ferric chloride. The solution is acidified with acetic acid, calcium acetate added, filtered, the filtrate containing the calcium salt acidified with sulphuric acid, and the aconitic acid extracted with ether. The aconitic acid so obtained melts after recrystallisation at 191°.

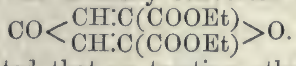
The authors point out that this synthesis is of importance in relation to the presence of aconitic and citric acids in nature.

E. C. R.

Hydrolysis of Ethereal Salts of Organic Acids by Potassium Acetate. By L. CLAISEN (*Ber.*, **24**, 127—128).—By the action of potassium acetate on ethyl oxalacetate, the triethyl salt of aconitoxalic acid is formed, and not the tetrethyl salt (see preceding abstract). Similarly, from ethyl acetonoxalate, the monethyl salt of diacetonedioxalic acid is formed instead of the diethyl salt. Hence potassium acetate, besides acting as a condensing agent, must also act as a hydrolysing agent. Ethyl oxalate (1 mol.), when warmed with a solution of potassium acetate (1 mol.) in an equal weight of water on the water-bath with constant shaking, is easily converted into potassium ethyl oxalate. Potassium oxalate is not formed in this reaction.

E. C. R.

Synthesis of Chelidonic Acid. By L. CLAISEN (*Ber.*, **24**, 111—120).—When an excess of ethyl oxalate reacts with acetone in the presence of sodium ethoxide, the sodium derivative of ethyl acetonoxalate, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot COOEt$, is first formed, and this, by the further action of ethyl oxalate and sodium ethoxide, is converted into the disodium salt of ethyl acetonedioxalate, $CO\cdot(CH_2\cdot CO\cdot COOEt)_2$. The latter is identical with ethyl xanthochelidonate, and is more stable than the acid, but is easily converted into ethyl chelidonate, or chelidonic acid,



$CO<\begin{matrix}CH:C(COOEt)\\CH:C(COOEt)\end{matrix}>O$.

It is to be noted that on treating ethyl acetonoxalate with ethyl oxalate, the ethyl oxalate residue enters the methyl group, and not the group $-CO\cdot CH_2\cdot CO-$. Probably other ethereal salts would give, with acetone, similar pyrone and xanthopyrone derivatives, and on treating these with ammonia, many new pyridine derivatives would be obtained. Ethyl acetonoxalate and ethyl acetonedioxalate correspond with the mono- and di-aldehyde derivatives of acetone. Compounds are easily prepared containing both an aldehyde and ethyl oxalate residue. Kerstiens has prepared such a compound by acting on acetone, first with an aldehyde then with ethyl oxalate. By heating, they are converted into derivatives of dihydropyrone. If, however, acetone be treated first with ethyl oxalate and then with an aldehyde, both the ethyl oxalate and aldehyde residues enter the same methyl group of the acetone, and a lactone is formed. The author restricts his attention to ethyl acetonedioxalate and its reactions, and reserves the last-named compounds for a later communication.

Ethyl acetonedioxalate (ethyl xanthochelidonate) is prepared by dissolving ethyl sodacetonoxalate (5 grams) in hot ethyl oxalate (8 grams), and adding to the hot mixture a solution of sodium ethoxide (2 grams) in alcohol (10 c.c.).

The product is washed with hydrochloric acid and water, and purified by crystallisation from alcohol. 350 grams of ethyl sodacetonoxalate yields about 320 grams of crude ethyl acetonedioxalate; this crystallises in slender prisms, melts at 103—104°, is somewhat easily soluble in hot alcohol, methyl alcohol, and benzene, and gives an intensely yellow solution with dilute alkalis. By prolonged boiling, it is partially converted into ethyl chelidonate. The alcoholic solution gives with ferric chloride an intense brown coloration, with ferrous sulphate a dark green; a greenish-yellow copper salt is precipitated by copper acetate, and a golden-yellow lead salt by lead acetate.

Chelidonic acid is obtained by heating the above compound with fuming hydrochloric acid, in a sealed tube, for one hour at 100°, or more easily by simply evaporating it a few times with fuming hydrochloric acid on the water-bath. It forms colourless needles, and gives all the reactions of natural chelidonic acid, but melts at 262° with charring and evolution of gas. The natural acid obtained from the celandine melts at 220°.

Ethyl chelidonate is obtained by saturating an alcoholic solution of ethyl xanthochelidonate with hydrogen chloride, and extracting the product with ether. It crystallises from alcohol in short, lustrous prisms, melts at 63°, and is crystallographically identical with ethyl chelidonate prepared from the natural chelidonic acid. E. C. R.

Oxidation of Gluconic Acid with Fehling's Solution. By W. Tiemann (*Chem. Centr.*, 1890, ii, 742—743; from *Zeit. Vereins Rübenzuckerind.*, 1890, 787—789).—The author's investigation was made with a view to determine whether gluconic acid is oxidised to glycuronic acid by Fehling's solution, such reactions being objectionable in the determination of sugar volumetrically. The author believes that the glycuronic acid is formed, although no very definite result was obtained. J. W. L.

Action of Nitric Acid on Ethyl Methenyltricarboxylate. By A. P. N. Franchimont and E. A. Klobbie (*Rec. Trav. Chim.*, **9**, 220—222).—Ethyl methenyltricarboxylate is prepared by the action of ethyl chloroformate on ethyl sodiomalonate; it boils at 149—150° under a pressure of 27 mm., and melts at 29°. It dissolves in nitric acid without development of heat, and on pouring the product into water an oily liquid separates of the composition $NO_2{\cdot}C(COOEt)_3$; this is decomposed by warming with barium hydroxide solution, yielding 3 mols. of carbonic anhydride. T. G. N.

Action of Nitric Acid on Methane Di- and Trisulphonic Acids. By A. P. N. Franchimont and E. A. Klobbie (*Rec. Trav. Chim.*, **9**, 223—224).—Although a nitro-derivative of methanedisulphonic acid is known to exist, the authors were unable to prepare nitro-derivatives by the action of absolute nitric acid on potassium methanedisulphonate and trisulphonate. T. G. N.

Preparation of Ethereal Salts of Furfuracrylic Acid. By L. CLAISEN (*Ber.*, **24**, 143—144).—Ethyl furfuracrylate is easily prepared by a method similar to that which has been employed by the author for the preparation of ethyl cinnamate (Abstr., 1890, 891). Sodium wire (1 mol.) is added to pure ethyl acetate (about 6 mols.), and furfuraldehyde (1 mol.) is gradually added to the well cooled mixture. When all the sodium has dissolved, acetic acid (1 mol.) is added, and then water. The salt is washed with soda, dried with calcium chloride, and distilled. It is a pale-yellow oil, and distils at 233—235° without decomposition. The acid prepared from it melts at 139—140° (compare Marckwald, Abstr., 1888, 135). By this method 25 grams of ethereal salt are obtained from 40 grams of furfuraldehyde.

This condensation takes place easily only in the case of acetic acid; when homologues of acetic acid are employed, the yield is less the greater the molecular weight of the acid. E. C. R.

Oxidation Products of Brominated Thiophens. By A. ANGELI and G. CIAMICIAN (*Ber.*, **24**, 74—78).—It has been shown by Ciamician and Zanetti (Abstr., 1890, 264, 1155) that whereas by the action of an alkaline solution of hydroxylamine, the pyrrolines are converted, with varying difficulty, into the dioximes of the corresponding γ-diketones, the same reaction does not take place with the thiophens. The authors find, however, that brominated thiophens are converted by concentrated nitric acid into open chain derivatives, a reaction corresponding with the conversion of brominated pyrrolines into dibromomaleïnimide (Abstr., 1887, 597; 1888, 61).

Tetrabromothiophen, when treated with nitric acid of sp. gr. 1·52, loses its sulphur and a portion of the bromine, and is converted into dibromomaleïc acid, $COOH\cdot CBr\dot{:}CBr\cdot COOH$. Tribromo-$\beta$-thiotolen, under similar conditions, yields the anhydride of bromocitraconic acid, $COOH\cdot CBr\dot{:}CMe\cdot COOH$, identical with the compound obtained by Fittig and Krusemark (Abstr., 1881, 416). α-Tribromothiotolen yields a compound having the composition $C_5H_4Br_2O_3$, which crystallises in small, colourless needles melting at 78—79°, and is probably *dibromacetylacrylic acid*, $CAcBr\dot{:}CBr\cdot COOH$. It is sparingly soluble in cold, readily in hot water, and in alcohol, ether, and benzene, the latter solution being precipitated by light petroleum. It gives a yellowish precipitate with phenylhydrazine consisting of fine, matted needles which appear to be a mixture, as the melting point lies between 84° and 100°. H. G. C.

Trithiënyl. By A. RENARD (*Compt. rend.*, **112**, 49—50).—Sulphur vapour and benzene do not react at a dull-red heat, but if the mixture is passed through a tube heated to bright redness, there is obtained, together with carbon bisulphide, hydrogen sulphide, and unaltered sulphur, a brownish liquid which, when distilled, yields unaltered benzene, and a yellow substance which soon solidifies. This last product is *trithiënyl*, $C_4SH_2(C_4SH_3)_2$, and after purification by repeated crystallisation from boiling alcohol, it forms yellowish needles melting at 147° to a yellow liquid which boils at 357°; vapour density 8·6. It is somewhat soluble in benzene, ether, and chloroform, but less soluble in alcohol, acetic acid, and light petroleum. When mixed with cold sulphuric acid, it becomes rose coloured, and on heating forms a violet solution which changes to blue. Water decolorises this solution, and precipitates unaltered trithiënyl.

Trithiënyl is not affected by boiling alkaline potassium permanganate, nor by ordinary nitric acid. The direct action of bromine in presence of carbon bisulphide yields *trithiënyl hexabromide*, $C_{12}S_3H_8Br_6$, as an unstable, black, amorphous powder which loses all its bromine when exposed to the air, and is instantly decolorised by cold alcohol, ether, and benzene. *Tribromtrithiënyl*, $C_{12}S_3H_5Br_3$, is obtained by the prolonged action of bromine at 100° in presence of acetic acid, and crystallises from benzene in slender, confused needles which melt at 282°, and are somewhat soluble in benzene, carbon bisulphide, and chloroform, especially when heated, but dissolve only slightly in acetic acid, and are insoluble in alcohol and ether. *Trithiënyltrisulphonic acid*, $C_{14}S_3H_5(HSO_3)_3$, is obtained by the action of fuming sulphuric acid at 115—120°; its calcium salt is not crystallisable, and forms a very soluble, brown powder.

A compound, $C_{12}H_8S_2O_4$, is obtained by the action of fuming nitric acid in sealed tubes at 150—160°, or by the prolonged action of chromic acid in a boiling acetic acid solution. In both cases the product is precipitated by water and crystallised from acetic acid. It forms white plates which melt at 312—313°, but do not boil even at 400°; it is insoluble in ether, carbon bisulphide, and light petroleum, very slightly soluble in benzene and chloroform, and slightly in acetic acid and in alcohol, especially on heating. Aqueous solutions of alkalis have no action on the compound, but it dissolves in nitric acid, and also in sulphuric acid at 100°, forming a colourless solution. It gives no characteristic coloration with sulphuric acid and isatin, or with phenanthraquinone. C. H. B.

Direct Substitution in the Aromatic Series. By C. A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, **9**, 210—219).—The author takes exception to the statement of Laubenheimer that, when the two nitro-groups of a dinitro-derivative have the meta- or para-position, one cannot be displaced by a hydroxyl- or amido-group, and suggests the following empirical law in reference to dinitro-derivatives:—When either the nitro-group or the chlorine or bromine atom occupies the ortho- or the para-position in reference to a second nitro-group, the former group or atom can be replaced by a hydroxyl-, alkoxyl-, or amido-group, whereas this substitution does not occur when the first nitro-group occupies the meta-position in reference to the second nitro-group. Numerous examples are adduced which confirm the above general conclusions. T. G. N.

Conversion of Orthochloronitrobenzene and of Orthobromonitrobenzene into Orthonitranisoïl and Orthonitrophenetoïl. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.* [3], 197—207).—Sodium alkyl oxides react with some halogen derivatives of benzene, substituting the alkoxide group for the halogen of the nucleus, and the author finds this reaction obtains in the cases of orthochloronitrobenzene and orthobromonitrobenzene.

To a solution of 1 : 2-orthochloronitrobenzene (3 grams) in methyl alcohol (15 c.c.) sodium methoxide (4 c.c. of a solution containing 0·0607 gram of sodium per c.c.) is added, and the mixture is heated in a sealed tube at 100° for six hours. After evaporation of the alcohol, the residue is treated with water, and the oily, yellow drops which separate are subjected to steam distillation, when nitranisoïl (2 grams) is obtained. The estimation of the chlorine in the residues proves the reaction to be quantitative.

1 : 2-Orthobromonitrobenzene when similarly treated, yields nitroanisoïl containing 4 per cent. of orthobromonitrobenzene.

When to a boiling mixture of orthochloronitrobenzene (2 grams) dissolved in alcohol (250 c.c.), sodium ethoxide (25 c.c. of a solution containing 0·0174 gram of sodium per c.c.) is added in successive portions of 15 c.c. and 10 c.c., an interval of 40 hours elapsing between the additions, there is obtained from the product of the reaction by treatment with weak aqueous soda and subsequent steam distillation, a yellowish-red liquid, which contains dinitrophenetoïl (80 per cent.) and unaltered orthochloronitrobenzene.

Orthobromonitrobenzene, when treated in like manner, yields a product which contains about 66 per cent. of phenetoïl.

From the above instances, the linkage of the chlorine atom to the benzene nucleus appears to be less strong than that of the bromine atom, which is a condition the reverse of that obtaining in the fatty series. T. G. N.

Unsymmetrical Trinitrobenzene (1:2:4). By C. A. Lobry de Bruyn (*Rec. Trav. Chim.* [3], 184—196).—Paranitrobenzene (40 grams) is heated with a mixture of nitric acid (sp. gr. 1·52) and sulphuric anhydride for six days, at a temperature which is gradually increased from 50—155°; the contents of the flask are then poured into cold water, and the mass, after washing, is treated with chloroform, and the yellow substance which this solvent extracts, is washed with weak sodium carbonate solution, dried, and distilled in a current of carbonic anhydride at 150°. By this means, any excess of paranitrobenzene is removed from the trinitrobenzene remaining in the retort, and it is purified by boiling with nitric acid (sp. gr. 1·4), from which it crystallises on cooling, and then recrystallising from ether, or from methyl or ethyl alcohol acidified with hydrochloric acid.

As thus obtained, trinitrobenzene (1 : 2 : 4) forms transparent, yellow crystals melting at 57·5°, and of sp. gr. 1·725—1·73 at 15·5°. It is very soluble in benzene, less so in chloroform, ether, methyl and ethyl alcohols, and but sparingly in carbon bisulphide (tables of solubility are given). The crystals enter into a condition of superfusion, and on evaporation of the chloroform or benzene solution it remains liquid for months, unless rubbed, when it solidifies.

By the action of a dilute solution of sodium methoxide in methyl alcohol, it is converted into dinitranisoïl (1 : 2 : 4), an almost quantitative yield being obtained, and a similar reaction obtains with sodium ethoxide; in this case some dinitrophenol is also formed, the yield depending directly on the concentration of the sodium ethoxide solution and on the temperature; thus, at the ordinary temperature with dilute sodium ethoxide solution, the yields corresponded with respective conversions of 74 per cent. and 62 per cent. of the tri-derivative into dinitrophenetoïl, and 4 per cent. and 6 per cent. into dinitrophenol; in the case of strong solutions at a higher temperature, 11 per cent. was converted into dinitrophenetoïl, and 60 per cent. into dinitrophenol.

Sodium hydroxide acts in a complex manner on the substance, but when it is heated with sodium carbonate solution, or with very dilute soda, dinitrophenol (1 : 2 : 4) is formed to the extent of 90 per cent. and 55 per cent. respectively of the trinitrophenol used.

Potassium cyanide and trinitrobenzene (1 : 2 : 4), dissolved in methyl alcohol, react at 25° to form dinitranisoïl.

When trinitrobenzene is heated in sealed tubes with methyl alcohol at 150° it yields dinitranisoïl, and similar treatment with water affords dinitrophenol (1 : 2 : 4). T. G. N.

Symmetrical Dinitrophenol. By C. A. Lobry de Bruyn (*Rec. Trav. Chim.*, **9**, 208).—Dinitranisoïl is prepared by heating solutions of trinitrobenzene (1 : 3 : 5), and of sodium methoxide in methyl alcohol at 80° for 30 minutes. The dinitranisoïl thus obtained as long, white needles melting at 105°, is heated with concentrated hydrochloric acid in sealed tubes at 170—180° for 5—6 hours, and the crystalline, reddish product is purified by pouring its solution in concentrated hydrochloric acid into water.

As thus obtained, θ-dinitrophenol forms silky needles, melts at 122°, is not attacked by dilute nitric acid, but dissolves in it, and crystallises out again in clear needles, whereas concentrated nitric acid (sp. gr. 1·4) forms with the substance a compound which melts at 173°. The author is continuing the research. T. G. N.

Metanitroparamidophenol and its Derivatives. By H. Hähle (*J. pr. Chem.* [2], **43**, 62—75).—Diacetylparamidophenol is best prepared by adding paramidophenol which has been dried quickly in a stream of hydrogen at 130—140° to double its weight of acetic anhydride, heating in a reflux apparatus for half an hour, distilling, and recrystallising the residue from water.

Nitrodiacetylparamidophenol is obtained by adding diacetylparamidophenol (1 part) by degrees to red fuming nitric acid (1½ parts) cooled by ice, and, when the liquid has become syrupy, pouring it into ice-cold water, and recrystallising the precipitate from alcohol. It forms brilliant, sulphur-yellow prisms which melt at 146—147°, and are decomposed at 260°; it is sparingly soluble in water, but more freely in glacial acetic acid, alcohol, and ether.

Metanitroparamidophenol (compare Hübner, Abstr., 1882, 506) is easily obtained by heating the diacetyl derivative with sodium hydroxide, and then precipitating with an acid. From ether it crystallises in dark-red prisms with a green lustre, melting at 148°, and from water in the same form with 1 mol. H_2O; it also dissolves in alcohol and chloroform. The *hydrochloride* and *sulphate* are described; also the *potassium* and the *tetramethylammonium* compounds. When the latter is heated, a small quantity of *nitroparanisidine* is formed; this crystallises in dark-red prisms, melts at 123°, dissolves in water, alcohol, and ether, sparingly in benzene, and volatilises with steam; its *acetyl* derivative melts at 115°; its *hydrochloride* is described.

Metanitroparadiazophenol chloride is obtained by passing nitrous acid through a cooled solution of metanitroparamidophenol, in alcohol containing some strong hydrochloric acid; it crystallises in colourless, microscopic prisms, explodes in a closed tube at 126—129°, and is sparingly soluble in water and alcohol, but insoluble in ether; the *perbromide* is described. When heated with absolute alcohol under pressure (790—800 mm.) it is converted into metanitrophenol; this settles the constitution of the above nitroamidophenol.

Metaparadiamidophenol (Köhler, Abstr., 1884, 1159), obtained by the usual reducing process, crystallises in colourless, microscopic prisms, and melts with decomposition at 167—168°; its hydrochloride is oxidised by ferric chloride to a red substance, probably a derivative of the red substance obtained by Griess, and others (Abstr., 1884, 1322; 1889, 500); its *sulphate* and *triacetyl*-derivative (melting at 135—136°) are described.

Metaparadiamidoanisoïl hydrochloride, obtained by reducing metanitroparanisidine, forms colourless, lustrous leaflets, dissolves in water with a brown colour, and yields a red colouring matter when oxidised.

Metanitropariodophenol is produced by the action of hydriodic acid on metanitroparadiazophenol chloride; it crystallises in yellow needles melting at 156°, dissolves in most solvents, and is not volatile with steam; the *potassium* and *silver* compounds are described; the *acetyl*-derivative melts at 107·5°, and begins to boil with decomposition at 260°. *Metanitropariodophenetoïl* forms microscopic, yellow needles, melts at 63·5°, and distils with decomposition at 320°. A. G. B.

Quantitative Investigation of Reduction Processes. By K. Elbs (*J. pr. Chem.* [2], **43**, 39—46).—An electric current was passed through a galvanometer, and then through a decomposing cell containing either an acid or alkaline solution of the substance to be reduced. The anode was separated from the cathode by a porous plate, and a tube was provided whereby the evolved hydrogen could be collected and measured. The electrodes were platinum foil of 15·6 sq.c. surface; the current was generated by 2—4 Bunsen's cells; the readings were taken every five minutes, and averaged on one hour.

The amount of hydrogen consumed in reducing the substance present is the difference between the amount actually evolved and the amount which should theoretically be evolved, as calculated from the intensity of the current shown by the galvanometer. The strength of the solution, the intensity of the current, the hydrogen liberated thereby, the hydrogen evolved, the hydrogen used in reduction, and the temperature are given in each experiment.

The substances experimented on were orthonitrophenol, paranitrophenol, orthoparadinitrophenol, and picric acid; they were dissolved in water or alcohol of different strengths, generally to the extent of 0·01 or 0·1 gram-molecule per litre; the quantity of sulphuric acid added was generally 2, but sometimes 4 gram-molecules; where sodium hydroxide was used, 2 gram molecules were added.

The author has not classified his results, and, inasmuch as nearly every condition varies in every experiment, it is difficult to see any relation between them. A stronger current does not bring about a proportionally greater reduction, a less percentage of hydrogen being consumed. Greater reduction occurs in alkaline than in acid solution. The order of reducibility of the substances experimented on is the same as that in which they are quoted above, the position of the nitro-group seemingly influencing it; for a general conclusion, however, the author requires a more extensive series of experiments.

A. G. B.

Phenol of Birchwood Tar. By M. PFRENGER (*Arch. Pharm.*, **228**, 713—719).—*Oleum betulini ætherium rectificatum* was the raw material employed; it is a brownish-yellow refracting liquid with acid reaction and sp. gr. 0·956 at 15°. The liquid was freed from acid by means of sodium carbonate, washed with water, and treated repeatedly with aqueous potash to obtain the phenoxide. From the latter, the phenol was separated by sulphuric acid, taken up with ether, well washed, and finally dried with sodium sulphate. The purified phenol was fractionated. After numerous operations, a fraction, 181° to 191, probably cresol with a small amount of phenol, was obtained. The fraction 191° to 200°, when heated with zinc-dust, yielded mainly toluene and a little anisoïl. The same fraction, when heated at 150° with methyl iodide and some methyl alcohol, yielded methyl cresyl ether and a little catechol dimethyl ether. The fraction 200° to 205° was dissolved in ether and heated at 80° with alcoholic potash; on cooling, the long needles of the potassium salt were collected, dissolved in water, and decomposed by hydrochloric acid, after which the separated compound was purified, and found to be guaiacol. The same fraction heated at 150° with methyl iodide yielded mainly catechol dimethyl ether and a little methyl cresyl ether.

The fraction 206° to 211°, when fused with potassium hydroxide, yielded, as the only definite product, hydroxyisophthalic acid. The fraction 218° to 224° gives the reactions of monomethyl homoxycatechol (creosol). The constituents of birchwood tar creosote are traces of phenol, cresol, guaiacol, 1.3.4-xylenol and 1.3.4-creosol, the third and last compounds forming the bulk.

J. T.

Constitution of Quinone. By F. KEHRMANN (*J. pr. Chem.* [2], **43**, 106—110).—It was a work of supererogation on the part of Nef to prove that the anilic acids contain two hydroxyl groups (Abstr., 1890, 1271), as this has already been generally accepted.

The tendency of quinone to form additive products with 2 and 4 atoms of bromine (*loc. cit.*), which enter in pairs into the ortho-position, is no better evidence for Fittig's than for Claus's formula for quinone. Analogy cannot be drawn between Baeyer's additive products of terephthalic acid and additive products of quinone, for the latter is an oxygen additive product, whilst hydroterephthalic acids are hydrogen additive products. The possibility that bromine may attach itself to the oxygen atom in quinone, and not to the carbon atom, must not be overlooked. A. G. B.

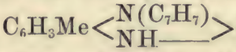
Colour Reactions of Aromatic Amines. By C. Lauth (*Compt. rend.*, **111**, 975—977).—The author has extended the reaction with lead peroxide to a large number of amines. One drop of a liquid amine, or an equivalent quantity of a solid, is mixed in a watch glass with 10 drops of a mixture of 3 vols. of acetic acid of 8° and 7 vols. of water. Fragments of lead peroxide are placed near the edge of the watch glass, and by inclining the latter the liquid is made to touch the peroxide. A similar experiment should be made with an alcoholic solution of acetic acid of similar dilution, since some of the bases are not soluble in aqueous acetic acid. The colour reactions in the second case are sometimes different, in consequence of the presence of oxidation products of the alcohol. The following results were obtained, the second series of colours being those obtained with the alcoholic solution:—

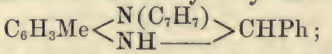
Aniline, very fugitive violet-red, changing to red-brown; with alcohol the same. *Methylaniline*, blue-green, violet, blue, olive; violet, red-violet, olive. *Dimethylaniline*, orange, grass-green, olive-green, grey; orange-green. *Ethylaniline*, blue-green, blue, violet, olive; violet, violet-black, olive. *Diethylaniline*, bright orange, yellow; greenish-yellow. *Benzylaniline*, red-brown, reddish-violet, grey; yellowish-grey, green. *Methylbenzylaniline*, orange, greenish-yellow, grey-green; bright green, blue-green, violet. *Ethylbenzylaniline*, orange; olive, bright green, olive. *Diphenylamine*, very faint violet-grey; bright green, olive. *Methyldiphenylamine*, magenta-red, violet, brown; violet-brown. *Paratoluidine*, bright blood-red, brown-red; bright blood-red. *Orthotoluidine*, dragon-green, violet; red-violet, brown-violet, orchil-colour. *Dimethylparatoluidine*, green-brown, dull yellow; green-brown, dull yellow. *Dimethylorthotoluidine*, bright orange-red, orange-brown; green-brown, olive. *Xylidine* (meta-α-, meta-β-, and a mixture of ortho- and para-), blue-violet, dark-grey; violet-red, orchil-colour. *Paraphenylenediamine*, bright blue-green, brown; bright blue-green, brown. *Metaphenylenediamine*, brown; brown. *Dimethylparaphenylenediamine*, magenta-red, blue-violet, violet-black; magenta-red, blue-violet, blue-black. *Dimethylmetaphenylenediamine*, faint yellow-brown; yellow-brown. *Toluylenediamine*, bright brown-red; bright brown-red. *α-Naphthylamine*, very faint blue-violet; very faint blue-violet. *β-Naphthylamine*, very faint brown-yellow; very faint reddish-brown. *Dimethyl-α-naphthylamine*, bright madder-red, opaque-white; madder-red, only slightly soluble. *Benzidine*, intense pure blue, violet, red; yellow solution and blue precipitate. *Tetramethylbenzidine*, grass-green, orange in presence of excess of acid; grass-green. *Dimethylorthoanisidine*, magenta-violet, dull violet; grey-green, olive. *Dimethylmetanisidine*, yellow-brown; yellow-brown. C. H. B.

Orthamidoparaditolylamine. By O. FISCHER and L. SIEDER (*Ber.*, **23**, 3798—3802).—*Orthamidoparaditolylamine*,

$$NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_7H_7,$$

is prepared by reducing orthonitroditolylamine (Abstr., 1882, 1059) with tin and hydrochloric acid, removing the tin with hydrogen sulphide, and precipitating the base with alkali. It crystallises from light petroleum in beautiful, colourless prisms, which quickly assume a brownish-red colour in the air; it melts at 109°, and dissolves in concentrated sulphuric acid with a beautiful, blue coloration, which changes to green on boiling or remaining for some time. The *hydrochloride* and *oxalate* crystallise in beautiful, colourless needles, the latter being almost insoluble in cold water. The *picrate*, $C_{14}H_{16}N_2,C_6H_3N_3O_7$, forms brownish-red crystals. On long-continued boiling with an excess of acetic anhydride, the diamine is converted into the *acetyl* compound, $C_{14}H_5N_2Ac$, which crystallises from alcohol in white prisms melting at 126°.

When an alcoholic solution of the diamine is boiled with carbon bisulphide for 8—10 hours, it is converted into the corresponding *thiocarbamide*,  $C_6H_3Me{<}\begin{smallmatrix}N(C_7H_7)\\ NH\text{———}\end{smallmatrix}{>}CS$, which is separated from a little adhering yellow colouring matter by repeated crystallisation from alcohol, and then forms colourless prisms melting at 270°. It is insoluble in water, sparingly soluble in light petroleum, readily in hot alcohol and benzene, and also soluble in concentrated sulphuric acid with a green colour.

The diamine condenses with aldehydes like other orthodiamines, forming anhydro-bases which may be regarded as derivatives of dihydroamidines. Benzaldehyde yields a compound having the constitution  $C_6H_3Me{<}\begin{smallmatrix}N(C_7H_7)\\ NH\text{———}\end{smallmatrix}{>}CHPh$; the crude, reddish-yellow, crystalline compound is purified by frequent crystallisation from alcohol with addition of animal charcoal, and then forms stellate groups of colourless needles, and melts at 156°. The *hydrochloride* forms long, colourless prisms; the *platinochloride*, $(C_{21}H_{20}N_2)_2,H_2PtCl_6$, orange crystals melting at 271°; and the *aurochloride*,

$$C_{21}H_{20}N_2,HAuCl_4,$$

golden-yellow needles. The anhydro-compound obtained from salicylaldehyde separates from alcohol in yellow crystals; it melts at 160°, and is sparingly soluble in water, alcohol, and hydrochloric acid, readily in benzene and hot dilute sulphuric acid. The orthonitrobenzaldehyde-derivative forms radiating, yellow crystals, and melts at 113°.

On addition of ferric chloride to a solution of the base in alcoholic hydrochloric acid, a blood-red solution is obtained, from which almost black crystals with a steel-blue lustre separate. These contain iron, and on treatment with ammonia assume a beautiful, red colour. The separated red flakes are carefully washed, dried, and extracted with benzene, which leaves hydrated ferric oxide as a residue. On concentrating the extract, or adding a little light petroleum, garnet-red, spear-shaped needles or narrow plates separate. This substance melts at 188°, decomposes on more strongly heating, and is fairly soluble in benzene, toluene, and boiling alcohol, sparingly in light petroleum. It is a feeble base, the salts of which are decomposed by water. Its formation is represented by the following equation:—$2C_{14}H_{16}N_2 + 2O = C_{28}H_{27}N_3O + NH_3 + H_2O$. Unlike the oxidation product of orthodiamidobenzene, its solutions show no fluorescence, and it appears to belong to a new class of compounds, of which the oxidation product of metaparatoluylenediamine is also a member. This has the composition $C_{14}H_{15}N_3O$, and crystallises from methyl alcohol in brownish-red crystals melting at 246—247°.

H. G. C.

Action of Phosphorus Chloride on Aromatic Tertiary Amines. By A. MICHAELIS and A. SCHENK (*Annalen*, **260**, 1—39; compare Abstr., 1888, 834).—*Paraphenylenedimethylaminedimethylphosphine*, $PMe_2\cdot C_6H_4\cdot NMe_2$, is obtained by gradually adding the theoretical quantity of dimethylamidophosphenyl chloride to zinc methyl, both compounds being previously dissolved in benzene, and the reaction being carried out in the cold and in an atmosphere of dry carbonic anhydride; the benzene is then distilled off in an atmosphere of carbonic anhydride, the residual zinc compound treated with excess of dilute soda, and the phosphine extracted with ether. It is a colourless, highly refractive liquid, boils at 265°, is lighter than water, and very readily oxidises on exposure to the air; it solidifies, when cooled, to a transparent, crystalline mass which melts at 10°.

Paraphenylenedimethylaminedimethylphosphine oxide,

$$POMe_2\cdot C_6H_4\cdot NMe_2 + H_2O,$$

is formed when the phosphine is exposed to the air, or, more quickly, when it is heated with finely divided mercuric oxide; it crystallises from hot ether in slender, colourless needles, melts at 62°, and is very readily soluble in alcohol and chloroform.

The *sulphide*, $PSMe_2\cdot C_6H_4\cdot NMe_2$, is best prepared by treating the phosphine with the theoretical quantity of sulphur in chloroform solution; it crystallises from hot alcohol, in which it is very readily soluble, in colourless needles, melts at 155°, and turns yellow on exposure to light.

The compound $PMe_2\cdot C_6H_4\cdot NMe_2,CS_2$ is produced by the direct combination of its constituents, the reaction being very energetic; it is a red powder, melts at 162°, and is sparingly soluble in alcohol.

Paraphenylenedimethylaminetrimethylphosphonium iodide,

$$PIMe_3\cdot C_6H_4\cdot NMe_2,$$

prepared by treating the phosphine with methyl iodide in well-cooled ethereal solution, crystallises from alcohol in colourless needles, melts at 264°, and turns yellowish on exposure to light.

The compound $PIMe_2Et\cdot C_6H_4\cdot NMe_2$, obtained by treating the base with ethyl iodide under the same conditions, crystallises in colourless needles, melts at 199°, and turns yellowish on exposure to light.

Paraphenylenedimethylaminediethylphosphine, $PEt_2\cdot C_6H_4\cdot NMe_2$, is formed when dimethylamidophosphenyl chloride is treated with zinc ethyl as described in the case of the corresponding dimethyl derivative. It is a colourless liquid, boils at 298°, and solidifies when cooled, melting again at 12·5°; it oxidises on exposure to the air, combines readily with bromine, and dissolves freely in hydrochloric acid, sulphuric acid, &c. The *oxide*, $POEt_2\cdot C_6H_4\cdot NMe_2 + H_2O$, prepared by heating the phosphine with mercuric oxide, crystallises from ether in thick, transparent needles, melts at 65°, and is very readily soluble in alcohol and chloroform. The *sulphide*, $PSEt_2\cdot C_6H_4\cdot NMe_2$, is a colourless, crystalline compound melting at 148°. The compound $PEt_2\cdot C_6H_4\cdot NMe_2,CS_2$ crystallises in small, red plates, melts at 107°, and is insoluble in ether, but soluble in alcohol and hydrochloric acid.

Paraphenylenedimethylaminediethylmethylphosphonium iodide,

$$PIMeEt_2\cdot C_6H_4\cdot NMe_2,$$

formed by the combination of the phosphine with methyl iodide, separates from alcohol in colourless crystals, melts at 186°, and is readily soluble in chloroform, but insoluble in ether. The corresponding *triethyl* derivative, $PIEt_3\cdot C_6H_4\cdot NMe_2$, is formed when the phosphine is warmed with ethyl iodide; it crystallises from alcohol in thick, colourless needles, melts at 180°, and is insoluble in ether, but readily soluble in chloroform.

Paraphenylenedimethylaminediphenylphosphine oxide,

$$POPh_2\cdot C_6H_4\cdot NMe_2,$$

is obtained when the corresponding phosphine (*loc. cit.*) is boiled with excess of ferric chloride; it separates from hot dilute alcohol in colourless, moss-like crystals, melts at 183·5°, and is readily soluble in alcohol, chloroform, and concentrated hydrochloric acid, but insoluble in water. The *sulphide*, $PSPh_2\cdot C_6H_4\cdot NMe_2$, prepared by boiling the phosphine with a carbon bisulphide solution of the theoretical quantity of sulphur, crystallises in slender, colourless needles, melts at 183°, and is readily soluble in alcohol and chloroform.

Paraphenylenedimethylaminediphenylmethylphosphonium iodide,

$$PIMePh_2\cdot C_6H_4\cdot NMe_2,$$

is a thick, yellowish oil; when treated with silver oxide in hot alcoholic solution, it is converted into a deliquescent, crystalline, strongly alkaline hydroxide, the *platinochloride* $(PPh_2\cdot C_6H_4\cdot NMe_2)_2,H_2PtCl_6$, of which separates from alcohol in orange plates.

Phenylenedimethylaminephenylmethylphosphine oxide,

$$POPhMe\cdot C_6H_4\cdot NMe_2,$$

is formed when a solution of the hydroxide just referred to, or of the corresponding iodide, is boiled with potash; it separates from a mixture of chloroform and light petroleum in compact crystals, melts at 146°, and is very readily soluble in most ordinary solvents.

Diethylamidophosphenyl chloride, $PCl_2\cdot C_6H_4\cdot NEt_2$, prepared as described in the case of the corresponding dimethyl compound (*loc. cit.*), is a thick, reddish oil, readily soluble in benzene, ether, and alcohol.

Methylbenzylamidophosphenyl chloride, $PCl_2 \cdot C_6H_4 \cdot NMe \cdot C_7H_7$, obtained in a similar manner, is a reddish oil, and resembles the diethyl-derivative in its properties.

Methylbenzylamidophosphinic acid, $P(OH_2) \cdot C_6H_4 \cdot NMe \cdot C_7H_7$, obtained by decomposing the sodium salt (see below) with dilute hydrochloric acid, crystallises from water or very dilute alcohol in small, slender needles, melts at 96°, turns greenish on exposure to the air, and is soluble in acids and alkalis. The *sodium* salt,

$$ONa \cdot P(OH) \cdot C_6H_4 \cdot NMe \cdot C_7H_7 + 2H_2O,$$

is deposited in colourless needles or plates when methylbenzylamidophosphenyl chloride is decomposed with water, the solution neutralised with sodium carbonate, evaporated to dryness, and the residue extracted with hot alcohol; it melts at 233°.

Ethylbenzylamidophosphenyl chloride, $PCl_2 \cdot C_6H_4 \cdot NEt \cdot C_7H_7$, prepared from ethylbenzylamine, is an oil.

Methylphenylamidophosphenyl chloride, $PCl_2 \cdot C_6H_4 \cdot NMePh$, is also an oil; when treated with concentrated soda, it solidifies to a mass of crystals of *sodium methylphenylamidophosphinate*,

$$ONa \cdot P(OH) \cdot C_6H_4 \cdot NMePh + 2H_2O.$$

This salt crystallises from alcohol in colourless, lustrous plates, melts at 265°, and is very readily soluble in water, but almost insoluble in benzene and chloroform. The corresponding acid,

$$P(OH_2) \cdot C_6H_4 \cdot NMePh,$$

crystallises from hot water in small needles and from alcohol in nacreous plates, and melts at 150·5°. F. S. K.

New Synthesis by means of Diazo-compounds. By R. HIRSCH (*Ber.*, **23**, 3705—3710).—The author, when preparing phenol by a synthetical method which has lately been used commercially, namely the decomposition of diazobenzene salts by boiling, has never obtained anything like a theoretical yield, and an examination of the bye-products led to the following results:—

If aniline hydrochloride is diazotised and the solution warmed until all the diazo-compound is destroyed, and then distilled as long as any trace of phenol comes over, the residue consists of a brownish liquid and a small quantity of resin, and deposits crystals after a time. These crystals were identified as parahydroxydiphenyl, $C_{12}H_{10}O$. Nitrohydroxydiphenyl is also formed in the reaction when an excess of nitrite is used, or when the diazo-solution is not allowed to remain long enough for the complete absorption of the nitrite. As it is probable that the hydroxydiphenyl is formed from phenol and diazobenzene, a solution of diazobenzene was shaken with phenol with the following results:—500 c.c. of diazobenzene solution, corresponding with 50 grams of aniline, was shaken with 500 grams of phenol containing 10 per cent. of water; the phenol solution increased in weight to 615 grams, and the aqueous solution contained only hydrochloric acid, sodium chloride, and phenol. The author supposes this phenol solution to contain oxyazobenzene, $C_6H_5 \cdot N_2 \cdot OC_6H_5$.

It evolves gas after a time in the cold, and decomposes violently on heating. It was cautiously decomposed in a reflux apparatus, and the phenol solution washed with strong salt solution and distilled. The portion boiling above 200° was mixed with twice its weight of toluene and extracted with 10 per cent. aqueous soda. The soda solution is coloured intensely blue and absorbs considerable quantities of oxygen. The product insoluble in soda, on distillation, gave, between 260° and 290°, diphenyl ether, OPh_2, to the extent of about 50 per cent. on the aniline used, and between 320° and 350° a neutral oil which is believed to be the ether, $C_{12}H_9{\cdot}OPh$.

The soda solution was covered with half its volume of toluene and acidified with constant shaking. On distillation of the toluene, a small quantity of phenol was obtained, and, between 260° and 300°, a mixture of parahydroxydiphenyl and orthohydroxydiphenyl to the extent of more than half the weight of aniline employed.

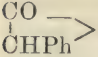
The blue compound, owing to the small yield, could not be isolated. It, however, forms an easily oxidisable leuco-compound, and behaves like a solution of paradihydroxydiphenylamine.

The author has obtained similar results with the homologues of aniline, and with benzidine and naphthylamine; and also when ortho-, meta-, or para-cresol is substituted for phenol. The phenols obtained give excellent yields of the corresponding hydrocarbons when heated with zinc-dust. On nitration in acetic acid solution, well crystallised nitro-compounds are formed. The description of the new compounds is reserved for a later communication.

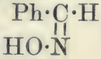
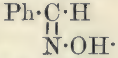
E. C. R.

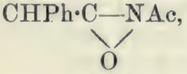
Action of Phenylhydrazine on α-Hydroxy-acids and their Ethereal Salts, II. By A. Reissert and W. Kayser (*Ber.*, **23**, 3701—3705).—The authors have already studied the action of phenylhydrazine on α-hydroxybutyric acid and mandelic acid (Abstr., 1890, 155); the present paper deals with the further study of the action of phenylhydrazine on mandelic acid and its ethereal salts.

When the reaction between mandelic acid and phenylhydrazine is brought about quickly (within an hour), pseudophenylhydrazidomandelic acid is formed; if, however, the mixture is heated for a day at 150°, a mixture of pseudophenylhydrazidomandelic acid and mandelic anilide is obtained, which cannot be separated by crystallisation.

Mandelic anilide, $OH{\cdot}CHPh{\cdot}CO{\cdot}NHPh$, obtained from the above mixture by extraction with acetic anhydride, melts at 146°, crystallises from water in beautiful, iridescent plates and dissolves easily in alcohol, ether, benzene, chloroform, and acetic acid, sparingly in light petroleum; this solvent precipitates it from its solution in benzene or chloroform. The ethyl salt of mandelic acid yields with phenylhydrazine the anhydride of phenylhydrazidophenylacetic acid,  $\begin{array}{l}CO\\ \vert\\ CHPh\end{array}\!>N_2HPh$ (which melts at 165—166°), together with varying quantities of pseudophenylhydrazidomandelic acid and benzylidenephenylhydrazine (m. p. 153°).

Dibenzoylpseudophenylhydrazidomandelic acid, $C_{28}H_{22}N_2O_4$, obtained by the action of benzoic chloride on pseudophenylhydrazidomandelic acid, crystallises from alcohol in colourless needles, melts at 208°, and is easily decomposed into benzoic and mandelic acids and phenylhydrazine. *Nitrosopseudophenylhydrazidomandelic acid*, $C_{14}H_{13}N_3O_3$, obtained by the action of nitrous acid on pseudophenylhydrazidomandelic acid, is very unstable, decomposes at about 70°, and is an acid whose salts with the heavy metals are extremely unstable. E. C. R.

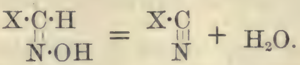
Determination of the Spacial Configuration of Stereoisomeric Oximes. By A. Hantzsch (*Ber.*, **24**, 13—31; see also Abstr., 1890, 348, 970, 1263, 1273).—I. *The Configuration of Stereoisomeric Aldoximes.*—In their first paper on the "asymmetrical nitrogen atom," Hantzsch and Werner, in agreement with the results of Goldschmidt, adopted the view that the two benzaldoximes are structurally identical, and that their isomerism is due to stereometrical causes, as represented by the formulæ,  $\begin{array}{c}\mathrm{Ph{\cdot}C{\cdot}H}\\ \|\\ \mathrm{HO{\cdot}N}\end{array}$ and  $\begin{array}{c}\mathrm{Ph{\cdot}C{\cdot}H}\\ \|\\ \mathrm{N{\cdot}OH}\end{array}$. The structural identity of these and similar oximes, which has been disputed by many chemists (Abstr., 1890, 1121, 1412), follows from the fact that the acetyl derivatives of the β-oximes are converted by traces of hydrogen chloride or of acetic chloride at the ordinary temperature into the acetyl derivatives of the α-oximes, whereas, as already frequently shown, hydrogen chloride has the reverse action on the oximes themselves, converting the α- into the β-compound. This is in full agreement with Hantzsch and Werner's formulæ, whereas, to explain it according to the formulæ given by Beckmann, namely,

$\mathrm{CHPh{\cdot}C{:}NOAc}$ and 

$$\mathrm{CHPh{\cdot}}\underset{\mathrm{O}}{\underset{\diagdown\ \diagup}{\mathrm{C{—}NAc}}},$$

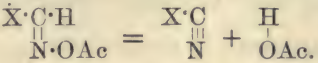
it is necessary to assume that a far reaching intramolecular change takes place, including a migration of the acetyl group from the nitrogen atom to the oxygen atom. Further, both α- and β-acetyl compounds are equally readily converted by soda or ammonia at the ordinary temperature into the original oximes, whilst, if in the one case the acetyl group were combined with oxygen, and in the other with nitrogen, some difference would almost certainly be noticed in their stability towards alkalis.

Hantzsch and Werner assigned to β-benzaldoxime the second of the formulæ given above, as it readily yields benzonitrile by loss of the elements of water. The validity of this argument was, however, disputed by Beckmann (Abstr., 1890, 1121), who maintained that benzamide is the first product of the reaction, and that this then loses water, forming the nitrile. The author, as is shown in detail in a subsequent abstract, finds that, in reality, benzonitrile is obtained directly, and that the benzamide found is really formed from the latter by the assumption of the elements of water. Moreover, not only β-benzaldoxime, but all β-aldoximes under certain conditions, readily yield nitriles at the ordinary temperature, whilst under the same circumstances the α-oximes yield no trace of nitrile. This reaction, therefore, affords a ready means of ascertaining to which group any particular oxime belongs, it being assumed in this, as in the case of maleïc acid, &c., that the groups between which the reaction takes place occupy an adjacent position in the molecule. The conversion of the β-aldoximes into nitriles is represented as follows:—



$$\begin{array}{c}X\cdot C\cdot H\\ \|\\ N\cdot OH\end{array} = \begin{array}{c}X\cdot C\\ \|\!|\\ N\end{array} + H_2O.$$

The β-oximes themselves do not usually pass directly into the nitriles, but their acetyl derivatives, which, as above stated, are reconverted by soda or ammonia into the original compound, are resolved by the alkaline carbonates into the nitrile and acetic acid:—



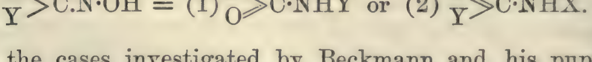
$$\begin{array}{c}X\cdot C\cdot H\\ \|\\ N\cdot OAc\end{array} = \begin{array}{c}X\cdot C\\ \|\!|\\ N\end{array} + \begin{array}{c}H\\ |\\ OAc.\end{array}$$

The isolation of the β-acetyl derivatives is a matter of considerable difficulty, although when once obtained in a condition of purity, they are fairly stable, and may be recrystallised from most indifferent solvents. As, however, the mere blowing of a little hydrogen chloride or acetic chloride vapour on to them is sufficient to convert them into the α-compounds, it is necessary to use acetic anhydride in their preparation, and to avoid all traces of mineral acids. For the simple determination of the configuration of an oxime, it is, however, unnecessary to isolate the acetyl derivative, the oxime being simply boiled with acetic anhydride, poured into iced water, filtered if necessary, and treated with solid sodium carbonate. The oil which separates is the acetyl derivative if the oxime is an α-compound, and the nitrile if it is a β-compound. The latter is detected by the odour and also by the fact that it does not dissolve in soda in the cold or on gentle warming.

II. *Configuration of Stereo-isomeric Ketoximes.*—Hitherto the only ketoximes concerning which any conclusion as to their configuration could be drawn, were those of the benzile group, no facts having been discovered which throw light upon the configuration of the stereoisomeric asymmetrical monoximes. The author now finds that this may be ascertained by a reaction which has long been known, namely, the conversion of the aromatic ketoximes into the isomeric acid anilides. Thus Beckmann found that benzophenoxime may be converted into benzanilide:—

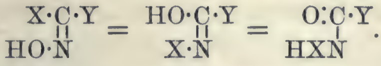
$$CPh_2{:}NOH = COPh\cdot NHPh.$$

With asymmetrical ketoximes, this reaction might take place in two different ways, as shown by the equation

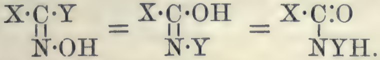


$$\genfrac{}{}{0pt}{}{X}{Y}{>}C{:}N\cdot OH = (1)\genfrac{}{}{0pt}{}{X}{O}{\gg}C\cdot NHY \text{ or } (2)\ \genfrac{}{}{0pt}{}{O}{Y}{\gg}C\cdot NHX.$$

In all the cases investigated by Beckmann and his pupils, the reaction proceeds in one and the same manner. As stereo-isomeric oximes were then unknown, the author has re-investigated this isomeric change with such isomerides, and finds that, in fact, the change takes place in a different manner in the two cases. Although the nature of this reaction is not yet fully understood, it appears probable that the hydroxyl combined with the nitrogen atom changes places with one of the groups combined with the neighbouring carbon atom, the tautomeric form of the acid amide containing the group $\mathrm{C(OH){:}N}$ being first formed. In the case of stereo-isomeric oximes, that radicle will change places with the hydroxyl which is nearest to it in space. With the formulæ employed by Hantzsch and Werner for the oximes, this intramolecular change is represented in the following manner:—

(1.) 

$$\begin{array}{c}\mathrm{X\cdot C\cdot Y}\\ \|\\ \mathrm{HO\cdot N}\end{array} = \begin{array}{c}\mathrm{HO\cdot C\cdot Y}\\ \|\\ \mathrm{X\cdot N}\end{array} = \begin{array}{c}\mathrm{O{:}C\cdot Y}\\ |\\ \mathrm{HXN}\end{array}.$$

(2.) 

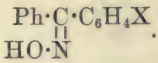
$$\begin{array}{c}\mathrm{X\cdot C\cdot Y}\\ \|\\ \mathrm{N\cdot OH}\end{array} = \begin{array}{c}\mathrm{X\cdot C\cdot OH}\\ \|\\ \mathrm{N\cdot Y}\end{array} = \begin{array}{c}\mathrm{X\cdot C{:}O}\\ |\\ \mathrm{NYH.}\end{array}$$

The behaviour of the benziledioximes likewise confirms this supposition, for β-benziledioxime, to which Hantzsch and Werner for other reasons assigned the constitution $\begin{array}{c}\mathrm{Ph\cdot C\cdot C\cdot OPh}\\ \|\ \ \|\\ \mathrm{H\cdot ON\ N\cdot OH}\end{array}$, is readily converted into oxanilide, whilst α-benziledioxime, which received the asymmetrical formula $\begin{array}{c}\mathrm{Ph\cdot C\text{———}C\cdot Ph}\\ \|\qquad\ \|\\ \mathrm{N\cdot OH\ \ N\cdot OH}\end{array}$, behaves in reality as an asymmetrical compound in Beckmann's reaction.

In the case of stereo-isomeric asymmetrical ketoximes, it is, therefore, possible to determine the configuration by means of the acid amide which it forms in Beckmann's reaction, the hydroxyl group being closer to that radicle which is found combined with the nitrogen in the amide. Thus, the two isomeric oximes of paramethoxybenzophenone, $\mathrm{NOH{:}CPh\cdot C_6H_4\cdot OMe}$, yield respectively anisanilide, $\mathrm{MeO\cdot C_6H_4\cdot CO\cdot NHPh}$, and benzaniside, $\mathrm{COPh\cdot NH\cdot C_6H_4\cdot OMe}$, in a pure condition. In most cases, however, it happens that only one of the oximes yields a pure product, the second giving a mixture of the two acid amides, owing to the fact that the labile oxime has in the reaction undergone a partial transformation into the more stable derivative. Thus, for example, the higher melting oxime of phenyl tolyl ketone yields pure paratoluylanilide, whilst the lower melting isomeride gives a mixture of the same compound with benzoparatoluidide, the latter being formed in larger quantity. The same holds good for the oximes of meta- and para-chlorobenzophenone. This reaction, therefore, also renders it possible to determine which is the stable, and which the labile, form. In most cases, the stable form is that in which the hydroxyl is nearest to the unsubstituted radicle, but in certain cases, such as paramethoxybenzophenone, the reverse is the case.

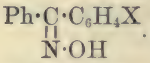
The nature of the acetyl derivatives of these oximes also corresponds exactly with the behaviour of the latter in the above intramolecular change, the stable forms yielding the stable acetyl compounds, whilst those giving a mixture of amides form acetyl derivatives which readily pass into the stereo-isomeride.

Hitherto it has not been possible to use any systematic nomenclature for the stereo-isomeric ketoximes, but in view of the above results, the author proposes to use the prefix α- for those in which the hydroxyl occupies the adjacent position to the unsubstituted phenyl or other radicle, and the prefix β- for those in which the hydroxyl and substituted radicle are adjacent, as shown in the formulæ:—



$$\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}C_6H_4X}\\ \quad\ \ \|\\ \mathrm{HO{\cdot}N}\end{array}.$$

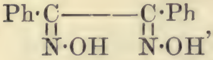
α-Ketoxime.



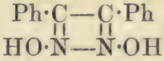
$$\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}C_6H_4X}\\ \quad\ \ \|\\ \quad\ \mathrm{N{\cdot}OH}\end{array}.$$

β-Ketoxime.

The benzilemonoximes and phenyltolyloximes then retain their present names; the three benziledioximes, however, which have the formulæ—

(α.) 

$$\begin{array}{ll}\mathrm{Ph{\cdot}C}\text{———}&\mathrm{C{\cdot}Ph}\\ \quad\ \ \| & \ \|\\ \quad\ \mathrm{N{\cdot}OH} & \mathrm{N{\cdot}OH}\end{array},$$

(β.) 

$$\begin{array}{ll}\mathrm{Ph{\cdot}C}\text{—}&\mathrm{C{\cdot}Ph}\\ \quad\ \ \| & \ \|\\ \mathrm{HO{\cdot}N}\text{—}&\mathrm{N{\cdot}OH}\end{array},$$

(γ.)

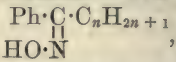
$$\begin{array}{ll}\mathrm{Ph{\cdot}C}\text{————}&\mathrm{C{\cdot}Ph}\\ \quad\ \ \| & \quad\ \ \|\\ \quad\ \mathrm{N{\cdot}OH} & \mathrm{HO{\cdot}N}\end{array},$$

become αβ-, αα-, and ββ-benziledioxime respectively.

In all the reactions mentioned in this paper, it appears that the hydroxyl group of the oxime takes part as a whole, and not simply the hydrogen atom of the group. This forms a strong argument against the proposals of Auwers and V. Meyer (Abstr., 1890, 1263).

H. G. C.

Configuration of Asymmetrical Oximes which do not form Stereometric Isomerides. By A. Hantzsch (*Ber.*, **24**, 31—36).—Hitherto stereometric isomerides have not been found in the case of the greater number of asymmetrical oximes; this may be due either to the fact that the "labile" form is too unstable to be isolated by any method as yet discovered, or to the fact that the hydroxyl group occupies a neutral position with respect to the groups X and Y, as in the formula $\frac{X}{Y}{>}\mathrm{C{:}N{\cdot}OH}$. Further, the known oxime might in reality be a mixture of the two isomerides in equal molecular proportions, similar to the optically inactive substances containing an asymmetric carbon atom.

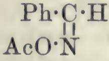
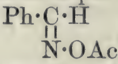
The author has subjected a number of these oximes to the reactions discussed in the previous abstract, and finds that all asymmetrical oximes correspond with one or other of the possible stereometrical formulæ, and that, therefore, the non-discovery of the second isomeride is due to the fact that it is so extremely unstable. The mixed aromatic ketoximes all have the α-constitution  $\begin{array}{l}\mathrm{Ph{\cdot}C{\cdot}C_nH_{2n+1}}\\ \quad\ \ \|\\ \mathrm{HO{\cdot}N}\end{array}$, for in Beckmann's reaction, it is always the aromatic group which migrates from the carbon to the nitrogen atom, as shown with acetophenone, deoxybenzoïn, and phenylacetic acid. The aliphatic ketoximes, on the other hand, are, as shown by Meyer (Abstr., 1886, 783), readily converted into nitriles by the action of acetic chloride, and must, therefore, be the β-isomerides. In the case of the ortho-substituted aromatic aldoximes, for which, at first, the β-constitution was considered most probable, it was found that their acetyl compounds may be reconverted into the oximes quite readily, and that they must, therefore, be α-derivatives.

Of very great interest is the behaviour of the thiophen-derivatives. The only known thiophenaldoxime corresponds very closely with β-benzaldoxime; it yields a nitrile by the action of acetic chloride, and is, therefore, really a β-compound. Thiënylglyoxylic acid also forms only a β-oxime, whilst it is found that phenylglyoxylic acid yields two, of which the β-compound is by far the more stable. It appears, therefore, that the α-configuration is stable with the aromatic aldoximes, but already labile with their carboxylic acids; it is rarely obtained in the thiophen-derivatives, and has not been found at all among the fatty compounds.

In all cases where a methyl group is present in the oxime, it appears to exert a repellent influence on the hydroxyl group, which then takes up a position adjacent to the second radicle.

H. G. C.

The Oximes of Aldehydes and α-Ketonic Acids. By A. Hantzsch (*Ber.*, **24**, 36—51).—The results given in this and the following paper form the experimental portion of the research of which the theoretical results have been discussed in the two preceding abstracts.

α-Acetylbenzaldoxime,  $\begin{matrix}\mathrm{Ph{\cdot}C{\cdot}H}\\ \|\\ \mathrm{AcO{\cdot}N}\end{matrix}$, is formed by the action of acetic anhydride on the oxime, and is an oil which is insoluble in solutions of alkaline carbonates, but is converted by ammonia and alkalis into the original oxime without forming a trace of nitrile. The action of acetic chloride on the oxime is less satisfactory, as the hydrogen chloride formed partially converts it into the β-oxime. *β-Acetylbenzaldoxime*,  $\begin{matrix}\mathrm{Ph{\cdot}C{\cdot}H}\\ \|\\ \mathrm{N{\cdot}OAc}\end{matrix}$, is only formed by very carefully adding a slight excess of acetic anhydride, gently warming, and pouring into iced water. The solution, on immediate evaporation in a vacuum, yields the acetyl compound in six-sided prisms; it melts at 55—56°, and is soluble in alcohol and benzene, sparingly in ether. When pure, it is fairly stable, but with cold soda or warm ammonia, it is reconverted into the β-oxime; with solutions of potassium or sodium carbonate, it yields benzonitrile, but, contrary to the observations of Beckmann (Abstr., 1890, 1121), the author has never been able to find any benzamide with the benzonitrile. It is converted into the α-acetyl compound by mineral acids, acetic chloride, bromine, iodine, &c., the change being instantly brought about by gaseous halogen hydro-acids, acetic chloride, and bromine:—By the action of acetic chloride on the β-oxime itself, one-half of the latter is converted into the α-acetyl compound, and the other into β-benzaldoxime hydrochloride.

The acetyl derivatives of α- and β-anisaldoxime are prepared in exactly the same manner. The former crystallises in oblique prisms melting at 48°, and the latter in four-sided prisms melting at 64°.

In their chemical behaviour also, they closely correspond with the acetylbenzaldoximes.

The oxime of phenylglyoxylic acid already prepared by Müller (Abstr., 1883, 1129) is not the primary product of the action of hydroxylamine. To obtain the latter, the action of hydroxylamine must be allowed to take place in the cold, and the solution then be extracted with ether. It separates from the latter in large, transparent, thick prisms, melts with complete decomposition at 127°, and is very soluble in water, alcohol, and ether. Its aqueous solution gives a characteristic, dark-green, voluminous precipitate with cupric acetate. It is converted by acetic anhydride into the *acetyl* derivative, OAc·N⁚CPh·COOH, which crystallises in oblique prisms, is soluble in alcohol, ether, and acetic anhydride, and decomposes at 118—119°; with alkalis and alkaline carbonates, it yields the original oxime, which has, therefore, the α-configuration. The β-phenyloximidoacetic acid, already obtained by Müller, is prepared by heating the acid with hydroxylamine in neutral, acid, or alkaline solution, or even by allowing them to remain together in the cold for several days. It crystallises in small, white needles, or four-sided, oblique prisms, melting when quite pure at 145° with evolution of gas, is less soluble than the α-compound in water, chloroform, and ether, and is very stable towards mineral acids, and even concentrated sulphuric acid; on long continued boiling with hydrochloric acid, or more readily with hydroxylamine hydrochloride, it is converted into benzonitrile. The β-acetyl compound is obtained with difficulty in six-sided tablets; it melts at 124—125° with decomposition, and passes very readily into benzonitrile and carbonic anhydride, thus confirming the supposition that the compound has really the β-configuration.

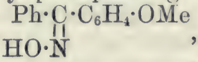
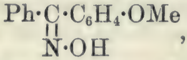
Like α-benzaldoxime, α-phenyloximidoacetic acid is converted into the β-compound by the action of hydrogen chloride on its dry ethereal solution, a very unstable hydrochloride of the latter being first formed. On the other hand, whereas β-benzaldoxime is reconverted into the α-compound by dilute aqueous hydrochloric acid, the reverse reaction takes place with the phenyloximidoacetic acid, the α- passing into the β-derivative. The latter may, however, be indirectly converted into the α-compound by the action of acetic chloride, which yields α-acetylphenyloximidoacetic acid.

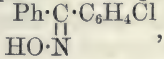
The only known oxime of thiophenaldehyde melts at 128°, and corresponds in its physical properties with β-benzaldoxime, and would, therefore, appear also to have the β-configuration. This is confirmed by the fact that not only the acetyl compound, but the oxime itself, readily passes into thiophen-nitrile on treatment with sodium carbonate solution. The *acetyl* compound, C_4H_3S·CH·NOAc, crystallises in oblique prisms melting at 75—80° with decomposition.

The oxime of thiënylglyoxylic acid has been prepared by Peter (Abstr., 1885, 765), and Bradley (Abstr., 1886, 1014), who describe it as crystallising in slender needles, and melting at 137°. After recrystallisation from dilute alcohol, the author found the melting point 145—146°, decomposition also taking place. It has also the β-configuration, and like β-phenyloximidoacetic acid is sparingly soluble in water; it passes even more readily than the latter compound into the nitrile when warmed with acidified water, or better with hydroxylamine hydrochloride. Its *acetyl* compound, which is best obtained by the action of acetic chloride, forms small prisms, melts at 85—87° with evolution of gas, and is converted into the nitrile not only by alkaline carbonates, but also by acetic acid, water, and alcohol.

The oxime of pyruvic acid, or methyloximidoacetic acid, has also the β-configuration. Its *acetyl* derivative, $CH_3\cdot C(NOAc)\cdot COOH$, crystallises in a similar manner to the oxime, melts at 60° with decomposition, and is converted by potassium carbonate at 0° into acetonitrile, carbonic anhydride, and water. H. G. C.

Stereo-isomeric Ketoximes. By A. HANTZSCH (*Ber.*, **24**, 51—61). As already explained, the configuration of the stereo-isomerides of asymmetrical ketoximes may be ascertained by their behaviour in Beckmann's reaction. The reagent employed was phosphorus pentachloride in absolute ethereal solution; the hydrolysis of the acid anilide formed was carried out by heating with concentrated hydrochloric acid at 160°.

Methoxybenzophenone, $COPh\cdot C_6H_4\cdot OMe$, is readily obtained by the action of benzoic chloride on anisoïl in presence of aluminium chloride, according to Gattermann's description (Abstr., 1890, 962). The action of hydroxylamine was carried out in alkaline solution, and the oximes separated by fractionally precipitating the acetic acid solution with water. The α-oxime,  $\begin{matrix}\mathrm{Ph\cdot C\cdot C_6H_4\cdot OMe}\\ \|\\ \mathrm{HO\cdot N}\end{matrix}$, separates generally as an oil, and crystallises from alcohol in four-sided, seemingly rhombic tablets melting at 137—138°. Its *hydrochloride* forms small needles melting at 123—124°, and its *acetyl* compound melts at 100°. Acetic chloride yields a mixture of the α- and β-acetyl compounds. In Beckmann's reaction, below −10° an anilide is formed which on hydrolysis yields aniline, methyl chloride, and phenol. Above −10°, some of the isomeric aniside of benzoic acid is also formed. The *β-oxime*,  $\begin{matrix}\mathrm{Ph\cdot C\cdot C_6H_4\cdot OMe}\\ \|\\ \mathrm{N\cdot OH}\end{matrix}$, is more readily soluble in organic solvents than the α-compound, and crystallises seemingly in rhombohedra. It forms a hygroscopic *hydrochloride* melting at 110°, and an *acetyl*-derivative melting at 52—53°. In Beckmann's reaction it is converted at all temperatures into the aniside of benzoic acid, which, on heating with hydrochloric acid, yields methyl chloride, paramidophenol, and benzoic acid. The β-configuration is, therefore, the more stable.

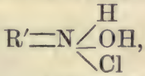
The oximes of parachlorobenzophenone were prepared and separated by the method given by V. Meyer. The α-oxime,  $\begin{matrix}\mathrm{Ph\cdot C\cdot C_6H_4Cl}\\ \|\\ \mathrm{HO\cdot N}\end{matrix}$, gave the anilide of parachlorobenzoic acid, whilst the β-acid, even at −10°, formed the parachloranilide of benzoic acid, mixed with parachlorobenzanilide. The α-compound is, therefore, here the stable modification.

The oximes of metachlorobenzophenone and the chloroketone itself have not hitherto been prepared. The latter is obtained by converting metamidobenzoic acid successively into metachlorobenzoic acid and its chloride, and acting with the latter on benzene in presence of aluminium chloride. It forms a crystalline powder sparingly soluble in alcohol and melts at 82—83°. The oximes were prepared in the usual manner and separated by fractional precipitation with water from acetic acid solution; the *α-oxime* is a crystalline powder which melts at 132—133°, and in Beckmann's reaction yields metachlorobenzanilide. The β-oxime melts at 105—106°, and gives in Beckmann's reaction at −20°, a mixture of the metachloranilide of benzoic acid and of metachlorobenzanilide. Here again, therefore, the α-derivative is the stable modification.

The oximes of paratolyl phenyl ketone have already been fully described. The α-oxime readily yields the anilide of paratoluic acid, and the β-oxime a mixture of two-thirds of the paratoluidide of benzoic acid and one-third of the anilide of paratoluic acid. β-Tolylphenylketoxime is, therefore, the most labile of the hitherto discovered labile modifications, which is probably due to the presence of the methyl group. It has also been found that the β-modification of parethylbenzophenonoxime is much more stable, and under suitable conditions may be converted solely into parethylbenzanilide.

In addition to the thiënylphenylketoxime, $C_4SH_3\cdot CPh{:}NOH$, discovered by Comey (Abstr., 1884, 1168), an isomeric compound is formed in the preparation of the oximes by Auwers' method, which is less readily soluble in the usual solvents and melts at 113—114°, the first compound melting at 91—92°. Both are readily converted into *acetyl* compounds, that obtained from the less fusible oxime melting at 88—89°, and that from the more readily fusible oxime at 80—84°.

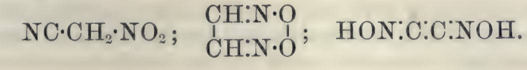
The Beckmann intramolecular change does not proceed smoothly with either compound, probably owing to the presence of the thiënyl group, and it has not, therefore, been found possible to determine which has the α-, and which the β-configuration.

The formation of two different hydrochlorides of stereo-isomeric methoxybenzophenonoximes mentioned above is of importance, inasmuch as it shows the existence of stereo-isomeric ammonium compounds of the general formula  $\mathrm{R'}{=}\mathrm{N}\begin{array}{l}\mathrm{H}\\ \angle\mathrm{OH}\\ \diagdown\mathrm{Cl}\end{array}$, which probably stands in close relation to the observation of Le Bel on certain differences in simpler structurally identical ammonium salts. H. G. C.

Constitution of Fulminic Acid: Dibenzoylcarbamide. By A F. Holleman (*Ber.*, **23**, 3742—3744).—When the dibenzoylcarbamide recently described (this vol., p. 64) is heated with 4 parts of aniline at 180—190°, it yields ammonia, benzamide, bezanilide, and symmetrical diphenylcarbamide; the relatively small quantity of ammonia and benzanilide is due to the fact that they are produced by the interaction of part of the benzamide with aniline.

The dibenzoylcarbamide from guanidine carbonate and benzoic anhydride melts at 197°, instead of 210°, as stated in text books, and is consequently identical with the symmetrical carbamide obtained from silver or sodium cyanamide.

The author considers fulminic acid to be a tautomeric compound represented by the following three formulæ, which readily serve to explain its reactions :—



$$NC\cdot CH_2\cdot NO_2;\quad \begin{matrix}CH{:}N\cdot O\\ |\qquad\ \ |\\ CH{:}N\cdot O\end{matrix};\quad HON{:}C{:}C{:}NOH.$$

J. B. T.

Hydroxyketones from Fatty Acids and Phenols. By A. Goldzweig and A. Kaiser (*J. pr. Chem.* [2], **43**, 86—98; compare Perkin, Trans., 1889, 546—549; Nencki, Abstr., 1890, 488).—*Propionylphenol*, $OH\cdot C_6H_4\cdot COEt$, is obtained by dissolving zinc chloride (2 parts) in propionic acid (1 part), adding phenol (1·5 parts), and heating until the liquid begins to boil (155°); the cooled mass is shaken with water and the undissolved portion recrystallised from hot water. It forms colourless needles or short, rhombic prisms; it is anhydrous and gradually becomes pale-yellow on exposure to light; it melts at 148° and dissolves in water (2896 parts at 15° and 30 parts at 100°), alcohol, and ether; its solutions are not coloured by ferric chloride, but they reduce ammoniacal silver solution in the cold. When melted with alkalis, it yields parahydroxybenzoic acid (m. p. 210°) and phenol. The *dibromo*-derivative, $C_9H_8Br_2O_2$, crystallises in leaflets which melt in a capillary tube at 100°, and are sparingly soluble in water, but freely so in alcohol and ether. *Propionyldinitrophenol* forms lustrous, yellow, anhydrous crystals which melt at 180°, and dissolve in hot water, alcohol, ether, and alkalis. *Propionylphenol hydrazone* forms yellow leaflets which melt at 80°; it is insoluble in water and is unstable therein; it dissolves in alcohol, ether, and benzene, and the solutions give precipitates with the salts of the heavy metals.

Propionylresorcinol, $C_6H_3(OH)_2\cdot COEt$ $[(OH)_2 : COEt = 1 : 3 : 4]$, is similarly prepared; it crystallises in lustrous, pale ruddy-yellow, slender needles, and melts in a capillary tube at 95°; it dissolves in alcohol, ether, benzene, and alkalis, but very little in water; it is coloured dark-red by ferric chloride but not by bleaching powder; its solution in water is precipitated by silver nitrate, lead acetate, and barium hydroxide; bromine precipitates it in weak alcoholic solution; its orientation is deduced from its analogy to orthoparadihydroxyacetophenone (resacetophenone). The *hydrazone* melts at 115° and is very unstable; it is similar in properties to propionylphenolhydrazone.

Propionylquinol, $C_6H_3(OH)_2\cdot COEt$, is prepared like propionylphenol; it crystallises in long, slender, lustrous, white needles, melts at 92° and is soluble in the same solvents as the above compounds; with ferric chloride, it gives a yellowish-red coloration; its solutions are precipitated by lead acetate and bromine-water, and reduce silver and copper solutions. The *hydrazone* melts at 100° and resembles the above hydrazones in properties.

Catechol does not form such ketones as the above, either with propionic or acetic acid; pyrogallol, on the other hand, yields them very easily.

Aceto-α-naphthol (α-hydroxynapthyl methyl ketone) has been described by Witt (Abstr., 1888, 486). *Propionyl-α-naphthol*, obtained by heating propionic acid (75 grams) with zinc chloride (100 grams) and α-naphthol (145 grams) and extracting with water and then with ether, forms yellow crystals which melt at 81°; it dissolves in sulphuric acid with an orange colour, and in alkalis with a yellowish-brown colour; it also dissolves in hot alcohol and ether, the solution in alcohol being coloured violet by ferric chloride. The *hydrazone* forms lemon-yellow crystals which are stable in air, melt at 128°, and dissolve in alcohol and ether. With diazobenzene chloride, propionyl-α-naphthol yields *propionyl-α-naphtholazobenzene;* this forms yellowish-red crystals which melt in a capillary tube at 110°.

Butyryl-α-naphthol crystallises in slender, grey, silky needles, melts at 78°, and is more soluble in water than the propionyl-derivative. *Isobutyryl-α-naphthol* melts at 79°. A. G. B.

Chloro-derivatives of Benzaldehyde. By H. Erdmann and E. Schwechten (*Annalen*, **260**, 53—78).—As the chloro-derivatives of benzaldehyde, some of which have recently been employed by Erdmann and Kirchoff for the synthesis of naphthalene derivatives (Abstr., 1889, 150), have as yet been but little investigated, and as many contradictory statements appear in the literature of these compounds, the authors have made them the subject of a more complete investigation.

The monochlorobenzaldehydes have, when pure, a pleasant odour, like that of oil of bitter almonds, but when boiled with water they give off irritating vapours.

Orthochlorobenzaldehyde (compare Erdmann and Kirchoff, *loc. cit.*) is best obtained in a pure condition by means of its oxime; it melts at −4·5 to −3°, boils at 213—214°, and gives orthochlorobenzoic acid on oxidation. The *oxime*, C_7H_6ClNO, is formed when the chloraldehyde is warmed with hydroxylamine hydrochloride and sodium carbonate in aqueous solution; it crystallises from alcohol in compact prisms, $a : b : c = 0·49926 : 1 : 0·48256$; $\beta = 85° 10'$, melts at 75—76°, and is reconverted into the aldehyde by boiling, dilute (1 : 1) sulphuric acid. The *hydrochloride* is gradually precipitated in large crystals when hydrogen chloride is passed into an ethereal solution of the oxime; it is soluble in ether and is reconverted into the oxime by cold sodium carbonate. The *acetal* is formed when chlorobenzaldehyde is boiled with acetic anhydride and sodium acetate; it crystallises from alcohol and chloroform, in which it is only sparingly soluble, in colourless needles, melts at 205—206°, and is reconverted into the aldehyde by boiling sodium carbonate.

Metachlorobenzaldehyde is best prepared by reducing metanitrobenzaldehyde (50 parts) with stannous chloride (225 parts) and concentrated hydrochloric acid (300 parts), gradually treating the ice-cold and diluted solution of the amido-compound with a solution of sodium nitrite (23 parts) in water (90 parts), and then decomposing the diazo-compound with a hydrochloric acid solution of cuprous chloride; when benzaldehyde is treated with chlorine in presence of zinc chloride as recommended by Müller (D.R.-P. 30329, 1883), both the meta- and the para-chloraldehyde are formed. Metachlorobenzaldehyde melts at 17—18° and boils at 213—214°. The *α-oxime*,

C_7H_6ClNO, obtained in the same way as the corresponding ortho-compound, crystallises from alcohol in large, pointed prisms, and melts at 70—71°.

Metachloro-β-benzaldoxime hydrochloride is gradually deposited in small, colourless crystals when hydrogen chloride is passed into an ethereal solution of the α-oxime; it melts between 130° and 140° with slight decomposition, and has a strong acid reaction. The *β-oxime*, prepared by decomposing the hydrochloride with sodium carbonate, crystallises from dilute alcohol in long prisms and melts at 115—116° when quickly heated, being converted into the α-oxime, a change which is analogous to that observed by Beckmann (Abstr., 1889, 607) in the case of β-benzaldoxime. Both the α- and the β-oxime of metachlorobenzaldehyde are decomposed by dilute sulphuric acid into the aldehyde and hydroxylamine.

Pure parachlorobenzaldehyde (compare Erdmann and Kirchoff, *loc. cit.*) melts at 47·5° and boils at 213—214°. The *α-oxime*, C_7H_6ClNO, is formed when the aldehyde is treated with hydroxylamine hydrochloride and sodium carbonate as described in the case of the ortho-compound; it separates from alcohol in colourless crystals, melts at 106—107°, and is very readily soluble in ether.

The *hydrochloride* of the β-oxime is obtained when the α-compound is treated with hydrogen chloride in ethereal solution; it crystallises in prisms, melts at 100—110° with slight decomposition, and has a strongly acid reaction. The *β-oxime*, prepared by decomposing the salt with cold sodium carbonate solution, crystallises from dilute alcohol in flat prisms, and melts at 140° when quickly heated, being at the same time converted into the α-oxime. The α- and the β-oxime are both readily decomposed by dilute sulphuric acid yielding hydroxylamine and parachlorobenzaldehyde.

Parachlorophenylisocrotonic acid, $C_6H_4Cl{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, is formed as an intermediate product in the conversion of parachlorophenylparaconic acid (*loc. cit.*) into 2- chloro-1′-naphthol, and is best prepared by carefully heating the paraconic acid in an oil-bath until the evolution of carbonic anhydride is at an end. It separates from carbon bisulphide in colourless crystals, melts at 108—109°, and when heated for some time at its boiling point is converted into the chloronaphthol mentioned above. The *sodium* salt,

$$C_{10}H_8ClO_2Na + 2H_2O,$$

crystallises from hot water, in which it is rather sparingly soluble, in colourless prisms.

The dichloro-derivatives of benzaldehyde can be prepared by chlorinating the corresponding dichlorotoluenes at their boiling points and then shaking the dichlorobenzal chloride (1 part), obtained in this way, with a mixture of concentrated sulphuric acid (2 parts) and fuming sulphuric acid (2 parts), containing 10 per cent. of sulphuric anhydride, until the evolution of hydrogen chloride is at an end; in the case of the compound of the constitution

$$[CHCl_2 : Cl_2 = 1 : 3 : 4]$$

the temperature must be raised to 30—40°, and in the case of the

1 : 2 : 3-compound to 40—50° in order to complete the reaction. The acid solution is finally separated from any undecomposed, insoluble chloride, poured on to ice, the crystalline aldehyde treated with sodium carbonate to free it from chlorinated derivatives of benzoic acid, and purified by distillation.

Dichlorobenzaldehyde [$CHO : Cl_2 = 1 : 2 : 4$], prepared from the corresponding dichlorotoluene, crystallises in colourless prisms, melts at 70—71°, boils at 231—245°, and has an odour like that of oil of bitter almonds. The *oxime* crystallises in long, silky needles, melts at 136—137°, and combines with hydrogen chloride in ethereal solution yielding a crystalline hydrochloride melting at 133·5°, which is reconverted into the oxime on treatment with sodium carbonate. The *acetal* crystallises in plates, melts at 221—222°, is only very sparingly soluble in the ordinary solvents, and is decomposed by soda.

The dichlorobenzaldehyde (m. p. 57—58°), described by Gnehm, (*Ber.*, **17**, 752), has the constitution [$CHO : Cl_2 = 1 : 2 : 5$]. It is volatile with steam, very readily soluble in most ordinary solvents, and dissolves in concentrated sulphuric acid with an olive-green coloration; on oxidation with potassium permanganate, it is converted into paradichlorobenzoic acid (m. p. 152—153°), from which paradichlorobenzene (m. p. 53—54°) can be easily obtained. The *oxime* crystallises from dilute alcohol in colourless needles, melts at 124—125°, and forms a crystalline hydrochloride which is very readily soluble in ether.

Dichlorobenzaldehyde [$COH : Cl_2 = 1 : 3 : 4$], prepared from the corresponding dichlorotoluene, melts at 43—44°, not at 68° as stated by Beilstein (*Annalen*, **152**, 229); it boils at 247—248°, is readily volatile with steam, and on oxidation it yields orthodichlorobenzoic acid (m. p. 201—202°). The *α-oxime*, $C_7H_4Cl_2{:}N{\cdot}OH$, crystallises from hot water in microscopic prisms and melts at 114—115°. The *hydrochloride* of the β-oxime is precipitated in crystals when hydrogen chloride is passed into an ethereal solution of the α-compound; it melts at 150° with decomposition, and is decomposed by sodium carbonate yielding the *β-oxime*. This compound crystallises from dilute alcohol in moss-like needles, and melts at 120° when quickly heated, being reconverted into the α-oxime.

2 : 4-*Dichlorophenylparaconic acid*, $C_{11}H_8Cl_2O_4$, can be obtained by heating the corresponding dichlorobenzaldehyde with succinic anhydride and anhydrous potassium acetate at 130—140° for 4—5 hours, as described in the preparation of chlorophenylparaconic acid (*loc. cit.*). It crystallises from hot water, in which it is only sparingly soluble (1 in about 140), in colourless plates, melts at 164·5—165·5°, and has a very bitter taste; the barium salt crystallises from hot water in prisms. The corresponding 2 : 5-*dichloro-acid*, $C_{11}H_8Cl_2O_4$, prepared in like manner, crystallises in colourless plates with 1 mol. H_2O, melts at 197—198°, and decomposes at 212° with evolution of carbonic anhydride. The 3 : 4-*dichloro-acid*, $C_{11}H_8Cl_2O_4$, crystallises from water in needles, melts at 136—137°, and decomposes at about 170° with evolution of carbonic anhydride.

2 : 4-*Dichlorophenylisocrotonic acid*, $C_{10}H_8Cl_2O_2$, can be obtained by

heating the corresponding paraconic acid in an oil-bath until the evolution of carbonic anhydride is at an end; it crystallises from carbon bisulphide in colourless prisms, melts at 120—121°, and on further heating is converted into 2 : 4-dichloro-1′-naphthol melting at 132° (compare Erdmann, Abstr., 1889, 265).

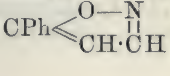
2 : 5-*Dichlorophenylisocrotonic acid*, prepared in like manner, crystallises from carbon bisulphide in colourless prisms, melts at 148—149°, and gives 1 : 4-dichloro-1′-naphthol when heated more strongly.

3 : 4-*Dichorophenylisocrotonic acid* is formed in small quantities when the corresponding paraconic acid is heated carefully, but the principal products are 1 : 2-dichloro-1′-naphthol and 1 : 3-dichloro-1′-naphthol; it crystallises in colourless needles, melts at 63—64°, and is only sparingly soluble in water. F. S. K.

Action of Hydroxylamine on Benzoylacetaldehyde. By L. Claisen and R. Stock (*Ber.*, **24**, 130—138).—The action of hydroxylamine on benzoylacetaldehyde differs in some respects from its action on 1 : 3-diketones, $\mathrm{R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R}$. The first product of the reaction is the monoxime, $\mathrm{CO{\cdot}Ph{\cdot}CH_2{\cdot}CH{:}NOH}$, whilst in the case of the diketones the reaction goes a step further; the elements of two molecules of water are eliminated, and an isoxazole is formed. The elimination of the elements of water from the monoxime of benzoylacetaldehyde takes place in two ways, according to the conditions; either cyanacetophenone or phenylisoxazole being formed. The latter is less stable than the isoxazole obtained from the diketone, and is slowly converted by aqueous alkali, instantly by sodium ethoxide, into the sodium salt of cyanacetophenone.

Benzoylacetaldoxime, $\mathrm{COPh{\cdot}CH_2CH{:}NOH}$, is obtained by adding a concentrated aqueous solution of hydroxylamine hydrochloride to the sodium salt of benzoylacetaldehyde, dissolved in seven times the weight of water and cooled to 0°. It crystallises in colourless prisms, melts at 86—87°, and is easily soluble in benzene, hot water, alcohol, methyl alcohol, ether, and chloroform, sparingly so in light petroleum and carbon bisulphide. It gives a bright yellow solution with alkalis, and is precipitated with carbonic anhydride; on the other hand, it dissolves to a noticeable extent in alkaline carbonate. Ferric chloride turns the alcoholic solution dark green, which is converted to a deep blue on the addition of sodium acetate; excess of sodium acetate precipitates a black iron salt.

Cyanacetophenone, $\mathrm{COPh{\cdot}CH_2{\cdot}CN}$, is prepared by mixing sodium benzoylacetaldehyde (17 grams) dissolved in water (100 c.c.) with aqueous soda (4 grams in 20 c.c.) and hydroxylamine hydrochloride (7 grams), and heating the mixture for a day on the water-bath. The oxime is also converted into cyanacetophenone by warming with acetic anhydride, and treating the product with soda. It crystallises from water in colourless, flat prisms and plates, resembling benzoic acid, melts at 80—81°, and is easily soluble in alcohol, but gives no coloration with ferric chloride. It dissolves in dilute alkalis and alkaline carbonates, and is reprecipitated by carbonic anhydride.

Phenylisoxazole,  $\mathrm{CPh}{<}\begin{array}{l}\mathrm{O{-}N}\\ \quad\;\,\| \\ \mathrm{CH{\cdot}CH}\end{array}$, is obtained when the above oxime is mixed with an equal weight of acetic chloride. The excess of acetic chloride is distilled off on the water-bath, and the oily product poured into cold dilute aqueous soda; the undissolved oil is extracted with ether, dried with calcium chloride, and purified by distillation. It is a colourless, crystalline mass, of characteristic odour, somewhat resembling that of benzonitrile, melts at 22—23°, boils at 246—248°, is easily soluble in alcohol, and gives no coloration with ferric chloride. By heating with dilute alkalis on the water-bath, it is converted into cyanacetophenone.

If a neutral mixture of sodium benzoylacetaldehyde and hydroxylamine hydrochloride in molecular proportion be warmed, a complicated condensation-product of the formula $C_{18}H_{17}N_3O_3$ is formed, $2C_9H_8O_2 + 3NH_2OH - 4H_2O = C_{18}H_{17}N_3O_3$. It is insoluble in alcohol, ether, light petroleum, chloroform, acetone, ethyl acetate, and benzene, crystallises from boiling amyl acetate in beautiful, white needles, melts at 197—198°, and is insoluble in aqueous soda.

An attempt to prepare an isoxazole by the action of acetic chloride on the oxime of salicylaldehyde, resulted in the formation of salicylamide, $OH{\cdot}C_6H_4{\cdot}CONH_2$. E. C. R.

Intramolecular Change in Unsaturated Acids. By R. Fittig (*Ber.*, **24**, 82—88).—Some years ago the author, in conjunction with Buri (Abstr., 1883, 485), showed that by the action of sodium amalgam on piperic acid, two different hydropiperic acids may be obtained by varying the conditions under which the action takes place, and that the *α*-acid is converted into the *β*-acid by simply boiling with aqueous soda. Further investigation (Abstr., 1887, 489) showed that the *α*-acid is a *βγ*-, and the *β*-acid an *αβ*-unsaturated acid. and the change is therefore similar to that observed by Baeyer and Rupe in the case of the hydroterephthalic and hydromuconic acids (Abstr., 1889, 1178; 1890, 875).

The author now finds that the conversion of *βγ*- into *αβ*-unsaturated acids by boiling aqueous soda is quite general. Thus cinnamenylpropionic acid,

$$CH_2Ph{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH, \text{ yields } CH_2Ph{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH,$$

crystallising from ether in thick plates which melt at 102·5°; phenylisocrotonic acid, $CHPh{:}CH{\cdot}CH_2{\cdot}COOH$, although less readily, yields the *αβ*-acid, $CH_2Ph{\cdot}CH{:}CH{\cdot}COOH$, which crystallises in plates melting at 65°; the aliphatic hydrosorbic acid,

$$CH_2Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH,$$

forms $CH_2Me{\cdot}CH_2{\cdot}CH{:}CH{\cdot}COOH$, which crystallises from hot water in long needles, melts at 33·5°, and boils at 216°.

As the *βγ*-unsaturated acids of any constitution may now be readily synthetically prepared (Abstr., 1890, 583), this reaction forms a ready method for the preparation of the *αβ*-unsaturated acids. The acids of the two series are readily separated by the fact that the *βγ*-unsaturated acids readily pass into the lactones on warming with dilute sulphuric acid, whilst the *αβ*-compounds remain unaltered.

The most natural explanation of this intermolecular change is that the $\beta\gamma$-unsaturated acid takes up the elements of water, forming the β-hydroxy-acid, and that the hydroxyl group then combines with the hydrogen atom in the α-position, re-forming water and the $\alpha\beta$-unsaturated acid. The experimental results do not, however, confirm this, for although the β-hydroxy-acids have been prepared, they do not appear to be intermediate products, but are more probably formed by the continued action of soda on the $\alpha\beta$-unsaturated acids. Further, the β-hydroxy-acids are remarkably stable; phenyl β-hydroxybutyric acid being partially volatile without decomposition, and scarcely attacked by boiling with soda for days. Phenyl-β-hydroxybutyric acid forms beautiful, flat needles melting at 98°, whilst the homologous phenyl-β-hydroxyvaleric acid forms lustrous prisms melting at 131°.

It can scarcely be doubted that α-hydropiperic acid, cinnamenylpropionic acid, and hydrosorbic acid all contain the group

$$\text{-CH}_2\text{·CH:CH·CH}_2\text{·COOH},$$

although they are all formed from acids probably containing the group -CH:CH·CH:CH·COOH, for Doebner has shown that the latter all yield racemic acid on careful oxidation (Abstr., 1890, 1274). This therefore confirms the conclusion of Baeyer, that the group -CH:CH·CH:CH·COOH passes, on partial reduction, into the group $\text{-CH}_2\text{·CH:CH·CH}_2\text{·COOH}$.

The author has also recently shown (Abstr., 1890, 894) that the ethereal salts of the paraconic acids are converted by the action of sodium ethoxide into the isomeric unsaturated itaconic acids, and is now investigating the properties of the latter to ascertain how far they correspond in properties with itaconic acid itself. The results obtained with methylitaconic acid have already been given; *ethylitaconic acid* is readily soluble in hot, sparingly in cold water, ether, chloroform, &c., and melts at 162—167°, losing water, and becoming yellow. On distillation, it passes into *ethylcitraconic anhydride; ethylcitraconic acid* is readily soluble in cold water, ether, chloroform, &c., crystallises well, and melts, when quickly heated, at 93—98°, but begins to decompose into anhydride and water at 70°, the same change taking place on boiling it with water. It is therefore volatile in a current of steam, and may thus be separated quantitatively from ethylitaconic acid. It is reconverted into the latter by heating its aqueous solution at 150°, but on boiling with nitric acid or treatment with bromine in chloroform solution, it yields *ethylmesaconic acid*, which has a solubility in water intermediate between that of its two isomerides, is readily soluble in ether, sparingly in chloroform, and melts at 174—175° without decomposition.

The salts of the three acids show great differences, but all, when reduced, yield propylsuccinic acid melting at 92°.

The properties of the three acids correspond closely with those of the initial members of the series, but the itaconic acid is much more stable, and is not so readily converted into its isomerides. The product of distillation obtained at the ordinary pressure contains 25 per cent. of itaconic anhydride. H. G. C.

Artificial Salicylic Acid. By W. R. Dunstan and O. F. C. Bloch (*Pharm. J. Trans.* [3], **21**, 429—436).—Artificial salicylic acid has been observed to differ in its therapeutic action from the pure "natural" acid obtained from the oil of winter-green. Although much work has already been done on the subject with the view of ascertaining the cause of this difference, the exact nature of the impurities contained in the artificial acid of commerce has not been experimentally established. The authors have examined two foreign acids, isolated by Williams in 1878 from commercial salicylic acid, but not then identified. These acids are now shown by their physical and chemical properties, as well as by the analyses of their silver and lead salts, to be orthocresotic or orthohomosalicylic acid [$CH_3 : OH : COOH = 1 : 2 : 3$], and metacresotic or metahomosalicylic acid [$CH_3 : OH : COOH = 1 : 3 : 4$] respectively. The ortho-acid melts at 163° (corr.), the meta-acid at 174·5° (corr.). They have been formed from the corresponding cresols contained in the crude phenol from which the salicylic acid had been prepared.

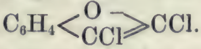
The melting point of pure salicylic acid has been variously stated, the highest recorded temperature being 159° and the lowest 155°. The authors find that "natural" salicylic acid, after recrystallisation from alcohol, melts at 156·75° (corr.), and that if the acid melting at this temperature be converted into the sodium salt, and fractionally precipitated with silver nitrate, the acid recovered from each fraction of silver salt also melts at 156·75°, which may therefore be accepted as the melting point of the pure substance. By very slowly cooling a 1 per cent. solution in hot water, the pure acid may readily be obtained in large, distinct, prismatic crystals, but in presence of about 5 per cent. of one of the cresotic acids, the salicylic acid no longer furnishes large crystals, and the impure acid melts at a lower temperature.

A specimen of the artificial salicylic acid of commerce (m. p. 154·5°) was examined by Williams' method. It was converted into a calcium salt by boiling with water and calcium carbonate, and crystallised many times from water. From the residue of soluble salt from which most of the calcium salicylate had crystallised, there was obtained a small quantity of an acid, which after further purification melted constantly at 151° (corr.). Analysis of the silver and lead salts, as well as its physical and chemical properties, proved it to be paracresotic or parahomosalicylic acid

$$(CH : OH : COOH = 1 : 4 : 3).$$

For the purposes of preparing pure salicylic acid from the impure acid of commerce, the method depending on the different solubilities of the calcium salts was not found satisfactory, being extremely tedious, owing to the number of recrystallisations that are necessary. A better plan consists in preparing the lead salts by the action of lead carbonate, and crystallising these from dilute alcohol; lead salicylate being much less soluble than the lead cresotates. By this means 70—80 per cent. of the original acid may be recovered in the form of pure salicylic acid from the first fraction of crystals deposited from the alcoholic solution.

At the request of the authors, Professor Charteris ascertained whether the three cresotic acids described above were poisonous. When administered in alcoholic solution to animals by injection, the ortho-acid was observed to be markedly toxic, the para-acid less so, whilst the meta-acid proved to be innocuous. W. R. D.

Coumarone. By A. R. L. DOHME (*Amer. Chem. J.*, **13**, 29—34; compare Fittig and Ebert, Abstr., 1883, 474; Rössing, Abstr., 1885, 388; and Kraemer and Spilker, Abstr., 1890, 496).—Aniline and concentrated ammonia are without action on coumarone even when heated with it in sealed tubes at 280°. Bromocoumarone, obtained by heating the dibromo-additive product with alcoholic potash, is also unaffected by these reagents. When coumarone and phosphorus pentachloride in molecular proportion are heated in sealed tubes at 175°, a mixture of coumarone dichloride and chlorocoumarone is obtained, and the latter, when heated at 275° with excess of pentachloride in a sealed tube for five hours, gives a compound which melts at 57·5—58°, crystallises in long, thin, white, satiny needles, and appears to have the constitution  $C_6H_4\left<\begin{matrix}O\\CCl\end{matrix}\right>CCl$. The remarkable stability of the coumarone molecule, and the difficulty with which the oxygen contained in it is replaced, both point to the conclusion that the closed-ring formula suggested by Fittig and Hantzsch correctly represents its constitution. G. T. M.

Quinonecarboxylic Acids. By J. STIEGLITZ (*Amer. Chem. J.*, **13**, 38—42).—*Tetrethyl parachloroquinonedimalonate*,

$$C_6Cl_2O_2[CH(COOEt)_2]_2,$$

is prepared by treating tetrachloroquinone (1 mol.) in dry benzene or acetone with ethyl sodiomalonate (4 mols.) dissolved in absolute alcohol. The reaction is complete after heating the mixture in a water-bath for a few minutes, and on acidifying, washing, drying, and evaporating the benzene solution, a dark oil is formed, which, when mixed with a little cold alcohol, deposits yellow needles. On recrystallisation from hot alcohol, pale yellow needles are obtained; these are only slightly soluble in ether or benzene, dissolve readily in chloroform and in hot alcohol, and with the alkaline hydroxides give deep violet-coloured solutions, due to the formation of compounds in which sodium or potassium is substituted for the remaining hydrogen atom in the malonic groups. Reducing agents, such as sulphurous anhydride or zinc-dust and glacial acetic acid, convert the compound into *tetrethyl paradichloroquinoldimalonate*,

$$C_6(OH)_2Cl_2[CH(COOEt)_2]_2.$$

This substance crystallises in white needles, melts at 160—161°, dissolves readily in ordinary solvents, gives a violet coloration with alkaline hydroxides, and is converted by oxidising agents, such as ferric chloride, into the quinone.

Tetrethyl paramidoquinonedimalonate, $C_6(NH_2)_2O_2[CH(COOEt)_2]_2$, crystallises in long, flat prisms, melts at 159—160°, and is formed when tetrethyl paradichloroquinonedimalonate is treated in the cold with alcoholic ammonia. It may be precipitated from its solution by means of water, and purified either by precipitation from its solution in chloroform by light petroleum or by simply washing it with ether.

Tetrethyl paradichloroquinonedimalonate is readily dissolved by a dilute solution of sodium hydroxide, the odour of alcohol being immediately perceptible. If, after remaining a few minutes, the solution be poured into cold sulphuric acid, a brown precipitate is formed, and this, on recrystallisation from acetone or alcohol, forms dark-red plates of *parachlorhydroxyquinone*, $OH\cdot C_6H_2ClO_2$; it sublimes with slight decomposition and without having previously melted, and is easily soluble in alcohol, in acetone, and in the alkaline hydroxides. If the solution of tetrethyl paradichloroquinonemalonate and sodium hydroxide be allowed to remain for an hour, and then warmed on a water-bath, both chlorine atoms are displaced by hydroxyl, the resulting compound agreeing in its properties with those ascribed to paradihydroxyquinone by Nietzki (Abstr., 1888, 1181) and Loewy (Abstr., 1886, 1028). The reaction by which the last-mentioned compounds are obtained consists in the substitution of hydrogen for the malonic groups; the author has consequently thought it of interest to commence the investigation of the action of ethyl sodiomalonate on ethyl dibromoquinoneterephthalate. The latter compound may be readily obtained from ethyl succinosuccinate by a simplification of the process used by Herrmann (Abstr., 1886, 1028) and Böniger (Abstr., 1888, 954). The succinosuccinate (1 mol.) is dissolved in dry chloroform, and bromine (1 mol.) gradually added; the chloroform solution is then shaken with an aqueous solution of sulphurous anhydride, dried, and evaporated on a water-bath. The crude ethyl dihydroxyterephthalate thus obtained is dissolved in warm glacial acetic acid and water (5—10 per cent. of the weight of the glacial acetic acid used), and three additional equivalents of bromine are added. On allowing the mixture to remain over night in a closed flask, ethyl dibromoquinoneterephthalate separates in crystals; a further quantity of it is precipitated on the addition of water (yield 84·5 per cent. of theory). G. T. M.

Indigo from Phenylglycocine. By K. Heumann (*J. pr. Chem.* [2], **43**, 111—112; compare this vol., p. 311).—The author does not question Lederer's observation that indigo is obtained when phenylglycocine is melted with sodium hydroxide, but he denies that it was published prior to the appearance of his own patent in the official journal. It has been known for 30 years and more that a "white" substance is formed when indigo is heated at 130—150° with melted potash containing a little water, and Biedermann and Lepetit have again drawn attention to the fact quite recently (this vol., p. 206). A. G. B.

Constitution of β-Benzopinacoline. By M. Delacre (*Bull. Soc. Chim.* [3], **4**, 470).—The author takes exception to the generally adopted formula for β-benzopinacoline, $CPh_3\cdot COPh$, which is based on the fact that by the action of alkali hydroxides and of oxidising agents it yields triphenyl-derivatives. Since on reduction it affords a hydrocarbon, $CHPh_2\dot{:}CHPh_2$, it should have a symmetrical constitution, and this is rendered probable since the alcohol obtained from β-benzopinacoline by the action of zinc ethyl yields by dehydration tetraphenylethylene, and the oxidation of this substance in acetic acid solution by potassium permanganate affords β-benzopinacoline, whereas by chromic acid it affords α-benzopinacoline. The author is about to work on this subject. T. G. N.

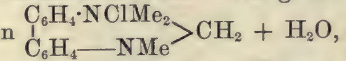
Derivatives of Dimethylaniline. By C. LAUTH (*Compt. rend.*, **111**, 886—888).—Twenty parts of dimethylaniline is dissolved in 120 parts of acetic acid of 8° and 160 parts of water, and 20 to 30 parts of pure lead peroxide is added gradually to the liquid, care being taken that the temperature does not exceed 30—35°. The reaction is complete in from 5 to 10 minutes, and the product is washed with warm water, boiled with water, dried, and crystallised from benzene. It is purified by crystallisation from petroleum, alcohol, or ether. The aqueous mother liquor, freed from lead by means of sulphuric acid and neutralised with ammonia, gives a further quantity of the product.

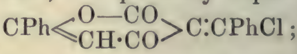
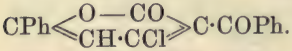
The product is tetramethylbenzidine, $C_{16}H_{20}N_2$, and the yield is about 40 per cent. of the dimethylaniline. In presence of acetic acid it gives an intense green coloration with lead peroxide. To obtain the pure colouring matter, 10 grams of the base, dissolved in 7·5 c.c. of hydrochloric acid and 200 c.c. of water, is added to 600 c.c. of a solution of ferric chloride of 45°, diluted with 540 c.c. of water. After some time, the mixture deposits the colouring matter in perfectly pure, microscopic crystals, which are washed with water, then with alcohol, and finally with absolute alcohol and ether. The mother liquors deposit a further quantity of the product when mixed with sodium chloride and acetate.

With more concentrated solutions, or with excess of ferric chloride, an acid combination of the orange and green products is obtained as a beautiful, orange precipitate, but prolonged washing with alcohol converts the orange compound into a green salt, which likewise contains iron. The crystals dissolve in water with a green coloration, which becomes orange on the addition of acids. Sodium chloride precipitates the unaltered compound from its solutions. Zinc salts also form a compound almost insoluble in saline solutions, but soluble in alcohol, from which it is precipitated by ether.

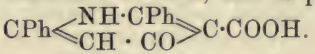
This product dyes silk a very pure green, but it is extremely unstable, and even out of contact with air and light the silk becomes colourless. It exists only in the form of salts, and is decomposed by cold water and very rapidly by hot water, with separation of a white compound. Alkalis produce the same result, with formation of hydrogen peroxide. In a dry vacuum, the green crystals decompose in about 24 hours, but they keep better in the air. When heated on a water-bath, they become colourless, with evolution of water and hydrogen chloride. In all these reactions the green colour does not reappear on neutralisation, but it forms again on treatment with lead peroxide.

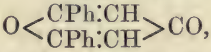
The crystalline green compound has the composition $C_{16}H_{21}ClN_2O$, and the white compound which separates in the various reactions is tetramethylbenzidine. The reaction with alkalis is represented by the equation $C_{16}H_{21}ClN_2O + NaOH = NaCl + C_{16}H_{20}N_2 + H_2O + O$.

A resinous product, which is probably a chlorine derivative of the base, separates at the same time. The green compound probably has the constitution  $\left.\begin{array}{l}C_6H_4{\cdot}NClMe_2\\ \vert \\ C_6H_4\text{——}NMe\end{array}\right>CH_2 + H_2O$, and is analogous to the product of oxidation obtained by Würster from tetramethylparaphenylenediamine. C. H. B.

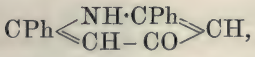
Dehydrobenzoylacetic Acid. By F. Feist (*Ber.*, **23**, 3726—3736; compare *Annalen*, **257**, 253).—Dehydrobenzoylacetic acid does not yield any ammonium salt; the compound $C_{18}H_{11}O_3Cl$, which is formed by the action of phosphorus pentachloride, and was termed by Perkin "chlorodehydrobenzoylacetic acid," is probably represented by one or other of the formulæ  $CPh\left<\begin{array}{c}O\text{—}CO\\ CH{\cdot}CO\end{array}\right>C{:}CPhCl$;  $CPh\left<\begin{array}{c}O\text{—}CO\\ CH{\cdot}CCl\end{array}\right>C{\cdot}COPh$. On treating this compound with sulphuric acid at 130—150°, *diphenylpyronecarboxylic acid*,

$$CPh\left<\begin{array}{c}O{\cdot}CPh\\ CH{\cdot}CO\end{array}\right>C{\cdot}COOH,$$

is obtained, which is isomeric with dehydrobenzoylacetic acid, and is deposited from benzene in small crystals melting at 201° with decomposition. The substance readily dissolves in chloroform, but is very sparingly soluble in water, dilute acids, or soda. The *ammonium salt* is crystalline and melts at 135°; the *barium salt* $(C_{18}H_{11}O_4)_2Ba + 6H_2O$, crystallises with difficulty; the *silver salt* forms an additive compound with silver nitrate; the remaining salts are amorphous. The acid gives a white precipitate with ferric chloride, which becomes pale-green after remaining for some time; with ferrous sulphate, a red precipitate is formed, changing to white and finally to violet-blue. On heating the acid, carbonic anhydride is eliminated, and 2—6-diphenylpyrone is formed (see below). By treating the acid with alcoholic ammonia at ordinary temperatures, a compound is obtained which melts at 237—240°, is insoluble in soda, and is probably *diphenylpyridonecarboxylic acid*,  $CPh\left<\begin{array}{c}NH{\cdot}CPh\\ CH\cdot CO\end{array}\right>C{\cdot}COOH$.

2 : 6-*Diphenylpyrone*,  $O\left<\begin{array}{c}CPh{:}CH\\ CPh{:}CH\end{array}\right>CO$, is prepared by heating dehydrobenzoylacetic acid with a large excess of concentrated hydrochloric acid in a sealed tube for 15 hours at 230—260°; it crystallises from benzene in colourless, slender needles, softens at 128°, melts at 138·5—139·5°, and is sparingly soluble in ether or alcohol at ordinary temperatures. The pyrone is almost insoluble in water or alkalis, but dissolves in concentrated sulphuric acid with a violet fluorescence, which is unaltered by heating.

Attempts to prepare a triketone by the action of barium hydroxide and hydrochloric acid, resulted in the formation of a small quantity of an impure compound, which crystallises in prisms and melts at 110° with decomposition. On heating dehydrobenzoylacetic acid with alcoholic ammonia in a sealed tube at 160°, *diphenylpyridone*,



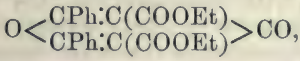
$$\mathrm{CPh}<\begin{matrix}\mathrm{NH\cdot CPh}\\ \mathrm{CH-CO}\end{matrix}>\mathrm{CH},$$

is formed; it is very sparingly soluble, and melts at 267°.

From the analogy thus shown to exist between dehydracetic acid and dehydrobenzoylacetic acid, it follows that the latter compound is really 6-phenyl-3-benzoylpyronone, and is represented by the formula $\mathrm{CPh}<\begin{matrix}\mathrm{O-CO}\\ \mathrm{CH\cdot CO}\end{matrix}>\mathrm{CH\cdot COPh}$. The two reduction compounds, $C_{18}H_{14}O_4$ and $C_{18}H_{12}O_3$, described by Perkin (Trans., 1885, 278), have probably one or other of the formulæ $\mathrm{CPh}<\begin{matrix}\mathrm{O-CO}\\ \mathrm{CH\cdot CO}\end{matrix}>\mathrm{CH\cdot CHPh\cdot OH}$ or $\mathrm{CPh}<\begin{matrix}\mathrm{O\text{———}CO}\\ \mathrm{CH\cdot CH(OH)}\end{matrix}>\mathrm{CH\cdot COPh}$, and $\mathrm{CPh}<\begin{matrix}\mathrm{O-CO}\\ \mathrm{CH\cdot CO}\end{matrix}>\mathrm{C{:}CHPh}$ or $\mathrm{CPh}<\begin{matrix}\mathrm{O-CO}\\ \mathrm{CH\cdot CH}\end{matrix}>\mathrm{C\cdot COPh}$ respectively.

J. B. T.

Ethyl Diphenylpyronedicarboxylate. By F. Feist (*Ber.*, **23**, 3736—3739; compare previous abstract).—*Ethyl cuprobenzoylacetate*, $\mathrm{(CHBz\cdot COOEt)_2Cu}$, is prepared by treating ethyl benzoylacetate with copper acetate, the liberated acetic acid being exactly neutralised with soda; it crystallises from benzene in small, green, lustrous needles, and melts at 180°; the yield is 50 per cent. of theory. By the prolonged action of carbonyl chloride in the cold on the copper compound, *ethyl* 2 : 6-*diphenylpyrone*-3 : 5-*dicarboxylate*,



$$\mathrm{O}<\begin{matrix}\mathrm{CPh{:}C(COOEt)}\\ \mathrm{CPh{:}C(COOEt)}\end{matrix}>\mathrm{CO},$$

is obtained; this crystallises in small, rectangular plates, melts at 140° with decomposition, and is sparingly soluble in water, dilute acids, or alkalis; the yield is very small. The compound gives no colour with ferric chloride, is entirely unacted on by heating with dilute sulphuric acid, and, on treatment with alcoholic potash, yields benzoic acid, acetic acid, acetophenone, and carbonic anhydride.

J. B. T.

Nitro- and Amido-derivatives of β-Naphthyl Ethyl Ether. By F. Gaess (*J. pr. Chem.* [2], **43**, 22—38).—1 : 2-Nitronaphthyl ethyl ether has been obtained by Wittkampf (Abstr., 1884, 1036).

3′ : 2-*Nitronaphthyl ethyl ether* is obtained by adding water to the mother liquor of 1 : 2-nitronaphthyl ethyl ether, and fractionally crystallising the precipitate from light petroleum; it is crystalline melts at 114°, and is very soluble in acetone, chloroform, and benzene, and sparingly in cold ether, alcohol, and petroleum; it is volatile with steam. By oxidation it is converted into β-nitrophthalic acid; this settles its constitution. It is not converted into the corresponding nitronaphthylamine when heated with alcoholic ammonia (compare *loc. cit.*).

1 : 2′-*Nitronaphthyl ethyl ether* exists in the resin which is thrown down by still further addition of water to the mother liquor of 1 : 2-nitronaphthyl ethyl ether, and is extracted therefrom by light petroleum, from which it is recrystallised several times It forms long, golden-yellow needles melting at 72—73°.

1 : 2-*Amidonaphthyl ethyl ether* crystallises in serrated tables, or in prisms and pyramids with reddish-blue fluorescence; it melts at 51°, and boils practically undecomposed at 300—302° (by Siwoloboff's method, Abstr., 1886, 497); it dissolves in the usual solvents. The *sulphate* and *hydrochloride* were obtained; the *acetyl* derivative melts at 145°.

3′ : 2-*Amidonaphthyl ethyl ether* crystallises in fluorescent pyramids, melts at 90—91°, boils at 330°, and dissolves in the usual solvents. The *hydrochloride* and *acetyl* derivative (m. p. 184·5°) were obtained.

1 : 2′-*Amidonaphthyl ethyl ether* crystallises in fluorescent prisms, melts at 67°, boils at 315°, and dissolves in the usual solvents. The *hydrochloride*, *sulphate*, and *acetyl* derivative (m. p. 139°) were obtained.

Two dinitronaphthyl ethyl ethers are obtained by treating 1 : 2-nitronaphthyl ethyl ether (1 part) with nitric acid of sp. gr. 1·42 (6 parts) at 0°, and separating by means of benzene.

Dinitronaphthyl ethyl ether (m. p. 144°) is easily soluble in benzene, and crystallises in yellow needles. When heated in a sealed tube at 180—190° with 20 times its weight of alcoholic ammonia, it yields a *dinitronaphthylamine* melting at 242°, and the dinitronaphthalene from this melts at 166—167°, but its orientation is not yet decided.

Dinitronaphthyl ethyl ether [$(NO_2)_2$: OEt = 1 : 1′ : 2] (m. p. 215°) is sparingly soluble in benzene, and crystallises in yellow needles; the corresponding dinitronaphthylamine melts at 223°, and the dinitronaphthol at 198°, with decomposition; the latter was converted into α-nitrophthalic acid (m. p. 160°, Abstr., 1882, 404), and this localises one of the nitro-groups, the other being ascertained by the conversion of the dinitronaphthylamine (m. p. 223°) into 1 : 1′-dinitronaphthalene (m. p. 170—172°).

When 3′ : 2-nitronaphthyl ethyl ether is nitrated, it yields 1 : 3′ : 2-dinitronaphthyl ethyl ether (m. p. 144°), which was described by Graebe and Drew (Abstr., 1884, 1036), and 1 : 2-nitronaphthyl ethyl ether yields the dinitro-derivative melting at 215° (see above).

A. G. B.

Naphthylene Dihydrosulphide and Dithiocyanate. By R. Ebert and E. Kleiner (*Ber.*, **24**, 144—147).—Naphthylene dihydrosulphide (dimercaptan) is best prepared by reducing disulphochlor-α-naphthalene [$(SO_2Cl)_2$ = 2 : 3′] dissolved in acetic acid with zinc-dust; the dimercaptan is then precipitated with water, and purified by converting it into the lead salt, decomposing this with hydrogen sulphide, and finally extracting the product with absolute alcohol. It is obtained as a snow-white, crystalline mass, which, on cautious heating, sublimes in glistening colourless scales, melts at 173—174°, and is soluble in ether, hot alcohol, benzene, carbon bisulphide, chloroform, and alkalis. The yield is about 5 per cent. of that required by theory. The *lead salt* is an orange-yellow powder which, like lead β-naphthylmercaptide, is precipitated together with lead acetate, and is obtained pure by boiling with water and washing with alcohol and ether.

Naphthylene dithiocyanate, $C_{10}H_6(SCN)_2$ [2 : 3′], is prepared by the action of cyanogen chloride on the above lead dimercaptide suspended in alcohol; it melts at 78°, is soluble in alcohol, ether, benzene, chloroform, carbon bisulphide, and acetic acid, and cannot be sublimed. When an alcoholic solution of the dithiocyanate is mixed with alcoholic potassium hydrosulphide, it is converted into the dimercaptan. When heated with fuming hydrochloric acid at 180°, it yields the dimercaptan, carbonic anhydride, and ammonia.

E. C. R.

Halogen Derivatives of β-Naphthylamine. By A. Claus and O. Philipson (*J. pr. Chem.* [2], **43**, 47—61).—By brominating β-naphthylamine, or its acetyl derivatives, only one monobromoderivative is obtainable, namely, 1 : 2-bromonaphthylamine melting at 63° (Cosiner, Abstr., 1881, 606); this is not a neutral substance, as Cosiner (*loc. cit.*) asserts, but is basic; its *hydrochloride* and *platinochloride* are described. When it is heated with acetic anhydride, *diaceto*-1 : 2-*bromonaphthalide*, $C_{10}H_6Br{\cdot}NAc_2$, is obtained; this crystallises in colourless tables which melt at 105° (uncorr.); on heating its alcoholic solution with aqueous ammonia, it is converted into aceto-1 : 2-bromonaphthalide (*loc. cit.*) melting at 140°.

1 : 3′-Dibromo-2-naphthylamine, m. p. 121° (Lawson, Abstr., 1885, 1239), is best prepared by adding bromine (2 mols.) to a cold solution of aceto-1 : 2-bromonaphthalide in chloroform, warming it after a time on the water-bath, until no more hydrogen bromide is evolved, and heating the acetyl derivative which separates with hydrochloric acid in alcohol; its *hydrochloride* is described. The acetyl derivative melts at 212° (uncorr.), not 208° (*loc. cit.*). The *diacetyl* derivative forms colourless, lustrous prisms melting at 180° (uncorr.). The orientation of this dibromonaphthylamine is settled by two facts; first, that its oxidation with nitric acid yields β-bromophthalic acid (1 : 2 : 5, m. p. 63°; Abstr., 1887, 668), showing that the second bromine atom occupies one of the β-positions in the ring which does not contain the NH_2 group; secondly, that the dibromonaphthalene obtained by removing the amido-group (see below) is not 1 : 2′-dibromonaphthalene (m. p. 75°; Abstr., 1889, 894), showing that the β-position occupied by the second bromine atom is 3′.

1 : 3′-*Dibromonaphthalene* is obtained by dissolving 1 : 3′-dibromo-2-naphthylamine (10 grams) in alcohol (100 grams), adding a mixture of sulphuric acid (12 grams) and alcohol (60 grams), cooling to 0°, and dropping into the agitated liquid the calculated quantity of sodium nitrite solution; after a time, the retort is heated until no more nitrogen is evolved, water added, and the mixture distilled with steam, when the new compound separates from the distillate in flocks which may be crystallised from alcohol. It forms pale-yellow needles melting at 61°, and is soluble in the usual organic solvents; it is perhaps identical with Jolin's dibromonaphthalene (this Journal, 1887, ii, 901). When oxidised with nitric acid, this dibromonaphthalene yields chiefly 4-bromoterephthalic acid (m. p. 106°), and only a little 3-bromophthalic acid.

By diazotising 1 : 3′-dibromo-2-naphthylamine in the usual way, the corresponding *diazochloride platinochloride* was obtained as a yellow, crystalline precipitate.

1 : 2 : 3′-*Tribromonaphthalene* forms colourless needles which melt

at 118°; it is little volatile with steam, sublimes in needles of the same melting point, and dissolves in alcohol, ether, and light petroleum.

1 : 3′-*Dibromo-2-chloronaphthalene* crystallises in long, slender, colourless needles, and melts at 102° (uncorr.); when the molten substance is quickly cooled, the melting point rises to 104—105°.

1 : 3′-*Dibromo-2-naphthonitrile* crystallises in slender, colourless, lustrous needles which melt at 178° (uncorr.), and dissolve in the usual organic solvents; it is sparingly volatile with steam; when heated for three days with 10 per cent. potash, it yields 1 : 3′-*dibromo-2-naphthoic acid* which crystallises in colourless, slender needles, melts at 245° (uncorr.), sublimes, and dissolves sparingly in water, but more freely in alcohol.

3′-*Bromo*-1 : 2-*naphthaquinone* is obtained by adding a cold solution of the above dibromonaphthalene diazochloride in small portions to boiling water, and heating until no more diazo-compound can be detected by sodium β-naphthol-α-disulphonate; the red colouring matter is collected, heated with water, and the solution cooled, when the quinone crystallises in yellow, feathery needles which darken at 100°, and melt with decomposition about 150°; it dissolves in the usual solvents when warmed, but not in sodium hydroxide solution. The corresponding *quinol* crystallises in soft, colourless needles, and decomposes without melting about 250°; it dissolves in warm chloroform and benzene; its solutions are coloured green by sodium hydroxide, and violet by ferric chloride; it reduces ammoniacal silver solution in the cold. These compounds are still under investigation.

Tribromo-β-naphthylamine, the orientation of which is being studied, is obtained by acting on a chloroform solution of 1 : 2-bromonaphthylamine with bromine (2 mols.) at a medium temperature, until no more hydrogen bromide is evolved, evaporating the solution, treating the residue with ammonia, and adding alcohol. It crystallises from a mixture of ether and alcohol in round, white, nodular aggregates, melts at 143° (uncorr.), and dissolves sparingly in alcohol and light petroleum, but freely in ether and chloroform. The *acetyl* derivative forms colourless, slender, feathery needles melting at 250—251° (uncorr.). The *diacetyl* derivative forms leaflets, and melts at 159° (uncorr.).

Attempts to obtain a series of chlorine derivatives corresponding with the foregoing bromine derivatives failed. When chlorine is passed into a cold chloroform solution of aceto-1-chloro-2-naphthalide, a *tetrachloracetochloronaphthalide*, $C_{10}H_6Cl \cdot NHAc,Cl_4$, is formed; this crystallises from ether or acetone in colourless prisms or needles which melt at 140—145° with decomposition; it cannot be crystallised from alcohol or chloroform, as these solvents decompose it, evolving hydrogen chloride.

1′ : 4′-*Dichloro-2-naphthylamine* is prepared by passing chlorine (2 mols.) into normal β-naphthylamine sulphate (1 part) suspended in 80 per cent. sulphuric acid (50 parts) until the solution has become lemon-yellow; the mixture is then poured into ice water, the precipitated flocks washed with dilute ammonia, and crystallised from alcohol, or distilled with steam. It crystallises from light petroleum in long, colourless needles which rapidly become coloured; it melts at 96° (uncorr.). The *acetyl* derivative forms large, colourless prisms melting at 209° (uncorr.). When this dichloronaphthylamine is treated with sulphuric acid and sodium nitrite, it is converted into 1′ : 4′-dichloronaphthalene (m. p. 68°), and when it is oxidised by dilute nitric acid, it yields 3 : 6-dichlorophthalic acid, whose anhydride melts at 183° (uncorr.); this acid is not identical with that obtained from dichlorortho-xylene, as stated by Beilstein (*Lehrbuch*, 2nd edition, **2**, 1160).

2 : 1′ : 4′-*Trichloronaphthalene*, melting at 69°, has been obtained, and is being investigated. A. G. B.

Formation of Quinalizarin from Alizarin. By C. Graebe (*Ber.*, **23**, 3739—3740).—Blue-green and green dyes are formed by heating alizarin-blue (dihydroxyanthraquinolinequinone) with concentrated sulphuric acid; the former of these compounds is found to be derived from the trihydroxy- and tetrahydroxy-quinones; the tetrahydroxy-compound may be readily purified, and is found to be identical with quinalizarin, to which Liebermann and Wense assigned the formula $C_6H_2(OH)_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2(OH)_2$ [OH : CO : CO : OH = 1 : 2 : 3 : 4; 3 : 6 : 4 : 5]. No phthalic acid is formed from the trihydroxy-derivative on oxidation. J. B. T.

Action of Sodium Benzyloxide on Cyanocamphor. By J. Minguin (*Compt. rend.*, **112**, 50—53).—When cyanocamphor is heated with benzyl alcohol and sodium in sealed tubes at 200°, the compound $CN{\cdot}CH_2{\cdot}C_8H_{14}{\cdot}COOC_7H_7$ is obtained, and after crystallisation from ether or, better, toluene, forms transparent lamellæ melting at 70—71°. It dissolves easily in cold benzene, toluene, and xylene, but is less soluble in ether, and in methyl, ethyl, and propyl alcohols. Its rotatory power in solution in toluene is $[\alpha]_D = +42{\cdot}8$. When treated with aqueous potash, or with concentrated hydrochloric acid, it yields hydroxycamphocarboxylic acid, $COOH{\cdot}CH_2{\cdot}C_8H_{14}{\cdot}COOH$.

The aqueous mother liquor from the preparation of this compound, when treated with an acid, yields a precipitate of the acid

$$CN{\cdot}CH_2{\cdot}C_8H_{14}{\cdot}COOH,$$

which crystallises from ether in distinct crystals melting at 164°, and somewhat soluble in ether and alcohol. Its molecular rotatory power in alcoholic solution is $[\alpha]_D = +64° 61'$. With aqueous potash, it yields hydroxycamphocarboxylic acid, with evolution of ammonia. The sodium salt, obtained by neutralising the acid with sodium carbonate, forms a white, gummy mass, very difficult to dry; the copper salt is a green powder which contains 1 mol. H_2O, and becomes blue when heated at 100°. The lead salt is anhydrous; the barium salt crystallises in needles containing 6 mols. H_2O. The silver salt blackens rapidly when exposed to light. C. H. B.

Action of Cyanocamphor on Sodium Phenoxide and Sodium Naphthoxide. By J. MINGUIN (*Compt. rend.*, **112**, 101—102).—Cyanocamphor, phenol, and sodium when heated in sealed tubes at 200—220° for 24 hours yield the compound $CN\cdot CH_2\cdot C_8H_{14}\cdot COOPh$, a viscous, brown oil, which boils with partial decomposition at 265—270° under a pressure of 40 mm.; rotatory power in alcoholic solution $[\alpha]_D = +26^{\circ}\cdot 66$. With aqueous potash, it yields ammonia, phenol, and hydroxycamphocarboxylic acid. The acid $CN\cdot CH_2\cdot C_8H_{14}\cdot COOH$ is found in the aqueous mother liquor from the crude product.

β-Naphthol, under the same conditions, yields an analogous compound, which crystallises in white crystals, soluble in benzene and toluene, but less soluble in alcohol and ether. With aqueous potash, it yields ammonia, naphthol, and hydroxycamphocarboxylic acid.

C. H. B.

The Presence of Ethylene Linkages in Terpenes. By V. MARKOVNIKOFF (*Ber.*, **24**, 67—70).—A reply to the communication of Wagner (*Ber.*, **23**, 2307), who attributes to the author views which he has never entertained.

Kuro-moji Oil. By W. KWASNICK (*Ber.*, **24**, 81—82).—Kuro-moji oil is the ethereal oil of *Lindera fericia*, Bl., one of the Japanese *Lauraceæ*, the use of which in Europe has largely increased of late. It is obtained from the leaves, and has a dark-yellow colour, a sp. gr. of 0·901 at 18°, and a powerful aromatic smell. Its small optical activity is due to the fact that it is a mixture of dextro- and lævorotatory constituents. By fractional distillation and treatment with sodium, it yields two terpenes, which have been identified by their derivatives as *dextrolimonene* and *dipentene*. In addition, two substances containing oxygen are present, namely, inactive terpineol and lævocarvole. The former has hitherto only been found in the oil of cardamon seeds and in kesso oil, obtained from a Japanese valerian. The carvole differs only from that obtained from cummin oil in possessing opposite optical properties. H. G. C.

Massoyene. By R. WOY (*Arch. Pharm.*, **228**, 687—690).—The existence of this terpene (Abstr., 1890, 638) has been disputed by Wallach (*ibid.*, 1316), who contends that the terpene described by the author is probably limonene, perhaps mixed with other terpenes. The latter obtained his results with a fraction boiling at 172°, whilst Wallach founds his criticism on results obtained with material boiling at 170—175°, the boiling point of limonene being 175—177°. The author hopes to publish the results of his further investigations on the terpenes of massoy bark shortly. J. T.

Ethereal Oils contained in Asafœtida. By F. W. SEMMLER (*Ber.*, **24**, 78—81; see also this vol., p. 322).—The second fraction obtained on distilling asafœtida in a vacuum, and which boils at 80—85° (9 mm.), has a sp. gr. of 0·9721 at 15°, rotates the plane of polarised light −12° 30′ with a column 100 mm. in length. Its composition is $C_7H_{14}S_2$, the vapour density being found as 165 and 164, instead of 162. The fraction is homogeneous, and boils at

210—212° (uncorr.) with slight decomposition under the ordinary pressure, and on distillation in a vacuum over small quantities of potassium, may be obtained as a perfectly colourless liquid boiling at 83—84° (9 mm.). It is a bisulphide, from which zinc-dust removes half the sulphur, and contains a saturated and an unsaturated radicle. It forms a *mercurochloride*, $C_7H_{14}S_2,2HgCl_2$, crystallising from alcohol in beautiful needles. When oxidised, it yields a deliquescent sulphonic acid, which has not been obtained pure. The bisulphide is present in the crude oil to the extent of 45 per cent.

The third fraction, boiling at 120—130° (9 mm.), has a sp. gr. of 1·0120 at 15°, and a column 100 mm. in length rotates the plane of polarisation $-18° 30'$. It decomposes on distillation under the ordinary pressure with evolution of most repulsive smelling gases. It has the composition $C_{11}H_{20}S_2$, the vapour density in an atmosphere of nitrogen being found to be 219 instead of the theoretical 216. It loses half its sulphur on treatment with zinc-dust, and is therefore also a bisulphide.

Notwithstanding the similarity between the odours of oil of garlic, oil of onions, and asafœtida, the latter contains no trace of allyl sulphide. The composition of the two former oils is now being investigated. H. G. C.

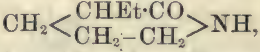
Suberin and Cork Cells. By F. A. Flückiger (and Gilson) (*Arch. Pharm.*, **228**, 690—700).—Kügler (1884) showed that suberin contained an appreciable amount of fat and extracted stearic acid; he also isolated the crystalline phellonic acid, which, however, does not belong to the fatty series. Gilson (1890) maintains that suberin is that part of cork texture which is insoluble in neutral liquids, and is not taken up either by concentrated sulphuric acid or by ammonio-copper oxide solution, but is dissolved by alcoholic potash, and with nitric acid yields suberic and other fatty acids soluble in ether and alcohol. He finds the colouring matter of cork to be very soluble in sodium carbonate solution, which scarcely attacks suberin even on prolonged boiling. After treating finely divided cork with sodium carbonate, the suberin is extracted by a 3 per cent. alcoholic potash solution. The solution filtered hot gives a precipitate on cooling, which, after washing with water and recrystallisation from alcohol, consists mainly of potassium phellonate. The alcoholic filtrate freed from alcohol, diluted with water, and treated with hydrochloric acid, gives a semi-fluid deposit; the decanted liquid yields glycerol. Gilson dissolves the deposit in ether, washes out the hydrochloric acid with water, expels the ether, dissolves in alcohol, and boils with potassium carbonate, when the addition of an alcoholic solution of magnesium chloride precipitates phloionic acid; the solution on further treatment yields suberinic acid. Kügler gives $C_{22}H_{42}O_3$ as the formula for phellonic acid, whilst Gilson prefers $C_{22}H_{43}O_3$. The latter gives the melting point as 102°. When heated at 105° with hydrochloric acid, the anhydride $C_{44}H_{84}O_5$ is obtained. *Phloionic acid*, $C_{22}H_{44}O_8$, is insoluble in cold water, but dissolves in hot water, forming crystalline needles on cooling; it is very soluble in alcohol, but only slightly in ether and in chloroform; it melts at 62—63°. *Potassium phloionate* is very soluble in ether, less so in alcohol. *Silver phloionate* is rapidly decomposed in the light, whilst the corresponding phellonate is only slowly coloured. *Magnesium phloionate* forms a crystalline precipitate when an alcoholic solution of a magnesium salt is added to a solution of phloionic acid. *Suberinic acid*, $C_{17}H_{30}O_3$, when gently warmed, forms a liquid miscible with alcohol, ether, and chloroform, but not with light petroleum. Its alkaline salts are soluble in water and alcohol; in the alcoholic solution no precipitate is produced either by magnesium or barium acetate. When heated without access of air, suberinic acid gradually forms a transparent, elastic mass, for which no solvent has yet been found. No water appears to be separated; the change appears rather to be due to polymerisation. *Potassium suberinate* is soluble in water and alcohol, but not in ether. The *silver* salt is rapidly decomposed. Gilson has observed a characteristic test for phellonic acid, which consists in the beautiful reddish-violet colour produced on moistening the acid with a very dilute, alcoholic iodine solution, and adding sulphuric acid (sp. gr. 1·8); the reaction succeeds best with potassium phellonate, and may be obtained with iodine in aqueous solution of potassium iodide, or with iodine in zinc iodide. The foregoing relates entirely to cork from *Quercus suber*. Gilson has, however, glanced at that from *Ulmus campestris* var. *suberosa*, and finds that this is much poorer in suberin. It yielded phellonic and suberinic acids, but neither phloionic acid nor glycerol. J. T.

Derivatives of Homopiperidinic Acid. By W. Aschan (*Ber.*, **23**, 3692—3701).—*Ethyl γ-phthalimidopropylethylmalonate*,

$$C_8H_4O_2{:}N\cdot[CH_2]_3\cdot CEt(COOEt) ,$$

is prepared by adding powdered γ-bromopropylphthalimide (11 grams) to a clear solution consisting of sodium (1·2 grams) dissolved in absolute alcohol (12 c.c.), and mixed with ethyl ethylmalonate (11 grams), and heating the mixture for some hours in a reflux apparatus. It crystallises from petroleum in short, colourless prisms, melts at 62° (uncorr.), and dissolves easily in alcohol, ether, benzene, chloroform, and carbon bisulphide, sparingly in light petroleum, and is insoluble in water.

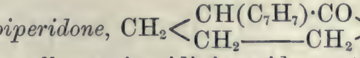
α-Ethylhomopiperidinic acid, $COOH\cdot CHEt\cdot[CH_2]_3\cdot NH_2$, prepared by heating the above compound with hydrochloric acid at 160° in a sealed tube, is easily soluble in water, insoluble in alcohol and ether, and melts at 200—200·5° (uncorr.) with frothing. The hydrochloride gives an *aurochloride*, which forms bright yellow, oily drops, crystallises when dried in a vacuum over sulphuric acid, and is very hygroscopic. The *platinochloride* is easily soluble.

β-Ethylpiperidone,  $CH_2<\begin{matrix}CHEt\cdot CO\\CH_2-CH_2\end{matrix}>NH$, obtained by distilling α-ethylhomopiperidinic acid under 42 mm. pressure at 140—142°, melts at 68° (uncorr.), has an odour resembling that of coniine, and is very easily soluble in all the usual solvents with the exception of petroleum; when crystallised from hot petroleum, it is obtained in thin, shining, colourless plates. The *aurochloride* is very hygroscopic, crystallises when dried in a vacuum, and dissolves easily in all the ordinary solvents. The *platinochloride* resembles the aurochloride.

Ethyl γ-phthalimidopropylbenzylmalonate,

$$C_8H_4O_2{:}N\cdot[CH_2]_3\cdot C(C_7H_7)(COOEt)_2,$$

prepared in a similar way to the corresponding ethyl compound, crystallises from 90 per cent. alcohol in flat prisms, and melts at 108—110°. When heated at 190—195° in a sealed tube with hydrochloric acid, it is converted into *α-benzylhomopiperidinic acid*, $NH_2\cdot[CH_2]_3\cdot CH\cdot(C_7H_7)\cdot COOH$, which melts at 195—196°, is easily soluble in hot water, only slightly in cold water or alcohol, and is insoluble in ether. It yields an *aurochloride* which crystallises in long, lemon-yellow prisms, melts at 102—103° without decomposition, and is very easily soluble in alcohol and ether, slightly in water; the *platinochloride* forms a microcystalline powder, decomposes on heating without melting, and is sparingly soluble in water, insoluble in alcohol and ether.

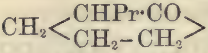
β-Benzylpiperidone,  $CH_2<\begin{matrix}CH(C_7H_7)\cdot CO\\ CH_2\text{——}CH_2\end{matrix}>NH$, obtained by distillation of α-benzylhomopiperidinic acid, crystallises from hot water in beautiful, thin plates of nacreous lustre, melts at 117—118°, and is insoluble in cold water, easily soluble in hot water, alcohol, ether, and benzene. The *aurochloride* forms viscous, oily drops, as also does the *platinochloride;* both are easily soluble in alcohol and ether. The *picrate* forms small, short crystals, melts at 97°, decomposes at about 150°, and is sparingly soluble in water.

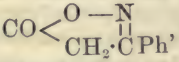
Nitroso-β-benzylpiperidone, $C_{12}H_{13}ON\cdot NO$, obtained by the action of potassium nitrite on β-benzylpiperidone dissolved in dilute sulphuric acid, crystallises from warm alcohol in beautiful, long prisms, melts at 61·5—62·5°, decomposes at about 100°, and is insoluble in water, sparingly soluble in cold alcohol and ether. When treated with excess of soda, nitrogen is evolved and ether extracts from the acidified solution α-benzyl-δ-hydroxyvaleric acid; this distils at 360°, and yields α-benzyl-δ-valerolactone, $C_{12}H_{14}O_2$, which forms a colourless oil having an odour resembling that of camphor and peppermint.

Ethyl γ-phthalimidopropylpropylmalonate,

$$C_8H_4O_2{:}N\cdot[CH_2]_3\cdot C(C_3H_7)\cdot COOEt,$$

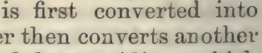
prepared in a similar way to the corresponding ethyl compound crystallises from methyl alcohol in oblong prisms, melts at 57° (uncorr.), and is insoluble in water, sparingly soluble in light petroleum, but easily in alcohol and ether. When heated with hydrochloric acid for four hours at 190°, it is converted into *α-propylhomopiperidinic acid*, $COOH\cdot CHPr\cdot[CH_2]_3\cdot NH_2$. The latter is soluble in alcohol, ether, petroleum, benzene, and water; from a mixture of water, alcohol, and ether, it crystallises in beautiful, colourless crystals belonging to the monoclinic system, $a : b : c = 1{\cdot}04145 : 1 : ?$; $\beta = 99° 41' 50''$, and melts at 186° (uncorr.) with frothing and partial decomposition. The *aurochloride* is not crystalline; the *platinochloride* crystallises in thin, yellow leaflets, melts at 206—209° with frothing and decomposition, and is insoluble in alcohol and ether, sparingly soluble in water.

β-Propylpiperidone,  $CH_2<\begin{matrix}CHPr\cdot CO\\CH_2-CH_2\end{matrix}>NH$, obtained by distilling α-propylhomopiperidinic acid under 40 mm. pressure at 156°, crystallises from light petroleum in snow-white needles, melts at 59° (uncorr.), and is easily soluble in the ordinary solvents. The *aurochloride* is very hygroscopic, and forms yellow, oily drops which partially solidify when dried in a vacuum or over sulphuric acid. The *platinochloride* resembles the aurochloride. Both salts are very easily soluble in alcohol and ether. E. C. R.

Phenylisoxazolone. By L. Claisen and W. Zedel (*Ber.*, **24**, 140—143).—*Phenylisoxazolone*,  $CO<\begin{matrix}O-N\\ \quad\;\|\\ CH_2\cdot CPh\end{matrix}$, is prepared by heating ethyl benzoylacetate (1 mol.), dissolved in 8 to 9 times its weight of glacial acetic acid, with finely-powdered hydroxylamine hydrochloride until the latter is dissolved. The greater part of the acetic acid is distilled off, the rest evaporated on the water-bath, and the product purified by crystallisation from alcohol. It melts at 147° with decomposition, is sparingly soluble in ether and cold alcohol, somewhat easily soluble in boiling alcohol, from which it crystallises in pale-yellow needles; it dissolves in dilute alkali and alkaline carbonates to a yellow solution, and is not reprecipitated by carbonic anhydride. The alcoholic solution reduces silver nitrate, and gives with ferric chloride a brownish-black coloration.

Isonitrosophenylisoxazolone is prepared by allowing a mixture of phenylisoxazolone, dissolved in the calculated quantity of normal soda and excess of sodium nitrite, to drop into well-cooled dilute sulphuric acid. It crystallises from hot water in bright-yellow, slender needles, melts at 143° with decomposition, is easily soluble in alcohol, ether, and acetic acid, and dissolves easily in alkalis and in alkaline carbonates to a light rose-red solution.

Benzeneazophenylisoxazolone, $C_3ONO{:}N\cdot NHPh$ or $C_3ONHO\cdot N_2Ph$, is obtained by adding a solution of diazobenzene chloride to an ice-cold solution of phenylisoxazolone in normal potash. It crystallises from alcohol in small, orange-yellow prisms, melts at 166°, and is easily soluble in ether, acetic acid, and hot alcohol. E. C. R.

Imido-ethers and their Derivatives. By A. Pinner (*Ber.*, **23**, 3820—3826).—In the hope of obtaining a new series of compounds, the author has investigated the action of ethyl imidobenzoate, $HN{:}CPh\cdot OEt$, on ethyl acetoacetate, but finds that the chief product is the same as that obtained from benzamidine under similar conditions, namely, *phenylmethylhydroxypyrimidine*,  $CPh<\begin{matrix}N-CMe\\N{:}C(OH)\end{matrix}>CH$. It is probable that the ethyl imidobenzoate is first converted into ethyl benzoate and ammonia, and that the latter then converts another portion of the imidobenzoate into alcohol and benzamidine, which unites with the ethyl acetoacetate.

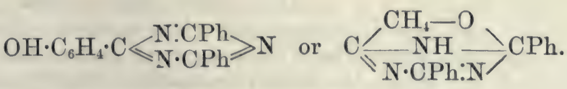
Formaldehyde acts readily on a solution of benzamidine in alcoholic ether at the ordinary temperature (compare this vol., p. 60), and, after a short time, a small quantity of cyanophenine separates. On adding water to the solution, a viscous liquid is precipitated which dissolves in hydrochloric acid, but quickly separates in beautiful prisms, an odour of formaldehyde being also observed. The same crystals are obtained directly by heating the amidine and formaldehyde at 100°. This substance, *methylenedibenzamide*, $CH_2(NH{\cdot}COPh)_2$, melts at 249·5°, is sparingly soluble in hot water and alcohol, and almost insoluble in acetone and chloroform. The first product of the reaction is probably the corresponding *di-imido-compound*,

$$CH_2(NH{\cdot}CPh{:}NH)_2,$$

which is decomposed by hydrochloric acid at the ordinary temperature and by water at the boiling point, with formation of methylenedibenzamide.

The compound obtained by the action of ethyl bromide and potash on dimethylhydroxypyrimidine (Abstr., 1889, 1007), to which the constitution $CMe{<}\substack{N\text{——}CMe \\ N{:}C(OEt)}{>}CH$ was assigned, really contains the ethyl group combined with the nitrogen atom, and has the formula $CMe{<}\substack{NEt{\cdot}CMe \\ N\text{——}CO}{>}CH$, corresponding with the compound described by E. v. Meyer (Abstr., 1881, 54), as the hydrobromide, on heating, remains unaltered, whilst the hydrobromides of pyrimidines containing the ethoxy-group, such as phenylmethylethoxypyrimidine, $CPh{<}\substack{N\text{—}CMe \\ N{:}C(OEt)}{>}CH$, lose ethyl bromide on heating, passing into the corresponding hydroxy-compounds.

The products prepared by treating ethyl salicylate and ethyl cresotate with benzamidine have been partially re-examined, and it has been found that the phenolic oxygen has not been displaced by nitrogen, as on heating the product from ethyl salicylate with hydrochloric acid at 130—150°, it is decomposed; the first products are doubtless benzamidine and salicylic acid, but these are further acted on, with formation of ammonia, benzamide, benzoic acid, phenol, and carbonic anhydride. For the constitution of this product, the author proposes the alternative formulæ:—



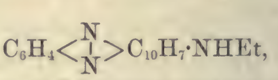
$$OH{\cdot}C_6H_4{\cdot}C{<}\substack{N{:}CPh \\ N{\cdot}CPh}{>}N \quad \text{or} \quad C{<}\substack{CH_4\text{—}O \\ \text{——}NH\text{——} \\ N{\cdot}CPh{:}N}{>}CPh.$$

As already shown by Glock (Abstr., 1889, 1290), paratolylmethylhydroxypyrimidine, $C_7H_7{\cdot}C{<}\substack{N\text{——}CMe \\ N{:}C(OH)}{>}CH$, is readily obtained by the action of tolenylamidine on ethyl acetoacetate. If ethyl ethylacetoacetate be substituted for the latter, the corresponding *paratolylmethylethylhydroxypyrimidine*, $C_7H_7{\cdot}C{<}\substack{N\text{—}CMe \\ N{:}C(OH)}{>}CEt$, is formed; it crystallises in hair-like needles, melts at 218°, and is insoluble in water, sparingly soluble in cold, fairly readily in hot alcohol. *Paratolylmethylbenzylhydroxypyrimidine*, $C_{19}H_{18}N_2O$, forms slender needles, insoluble in water, sparingly soluble in boiling alcohol, readily in pyridine, and melts at 240°. *Paratolylphenylhydroxypyrimidine*, $C_{17}H_{14}N_2O$, obtained from ethyl benzoylacetate, also forms slender needles melting above 290°. H. G. C.

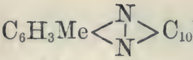
Phenazines. By K. Eicker (*Ber.*, **23**, 3803—3810).—An extension of the synthesis of phenazine derivatives, described by O. Fischer and Hepp (Abstr., 1890, 801, 1444), to other azo-colouring matters, the latter being prepared by the method also given by Fischer and Hepp (Abstr., 1890, 908).

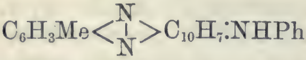
Benzeneazo-α-ethylnaphthylamine crystallises from a mixture of ether and light petroleum in red, prismatic crystals with a bluish reflex, which, after frequent recrystallisation, melt higher than previously stated, namely, at 88°. Its *hydrochloride* forms reddish-violet needles, melts at 181°, is sparingly soluble in alcohol, and partially dissociated by water. *Benzeneazo-α-dimethylnaphthylamine* is obtained by the action of diazobenzene chloride on α-dimethylnaphthylamine, and forms a scarlet syrup with a bluish reflex, which has not been obtained crystalline. Its *hydrochloride* forms thin, indigo-blue needles melting at 105°.

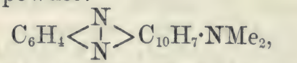
α-Ethylamido-α-naphthaphenazine,

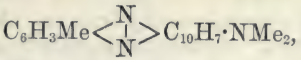


$C_6H_4{<}\overset{N}{\underset{N}{|}}{>}C_{10}H_7{\cdot}NHEt$, is prepared by heating orthodiamidobenzene and benzeneazoethylnaphthylamine hydrochloride, in molecular proportion, with double the quantity of absolute alcohol at 140° for 5—6 hours. The separated crystalline mass, which consists chiefly of the new base, is washed with water and dilute alcohol, and recrystallised twice from alcohol. A larger quantity is contained in the liquid portions of the tube contents, and is isolated by precipitating with water, dissolving in dilute alcoholic hydrochloric acid, reprecipitating with sodium acetate, and repeatedly crystallising the hydrochloride. The base is insoluble in water and alkalis, sparingly soluble in ether, benzene, and cold alcohol, and still less so in chloroform, the solutions showing a beautiful, yellowish-green fluorescence. It separates from benzene on the addition of light petroleum as a yellow, crystalline powder, and sublimes in yellow, woolly needles, partially carbonising at the same time. Its salts crystallise well, and show a metallic lustre, the solution having a magenta colour, and readily dissociating when warmed. The *hydrochloride* forms garnet-red needles with a coppery lustre; the *platinochloride*, $(C_{18}H_{15}N_3)_2,H_2PtCl_6$, is a scarlet precipitate, consisting of microscopic slender needles; whilst the *aurochloride*, $C_{18}H_{15}N_3,HAuCl_4$, is a red, microcrystalline powder, sparingly soluble in alcohol. The *nitrate*, $C_{18}H_{15}N_3,HNO_3$, crystallises from alcohol in brownish-red, slender needles which have a metallic lustre; and the *acetyl* compound, $C_{18}H_{14}N_3Ac$, crystallises from acetic acid in very sparingly soluble, straw-yellow, rhombohedral crystals. On heating with concentrated hydrochloric acid at 175—180°, α-ethylamidonaphthaphenazine is converted into ammonia, alcohol, and the α-hydroxynaphthaphenazine already described by Fischer and Hepp (*loc. cit.*).

α-Ethylamido-α-naphthatolazine,  $C_6H_3Me<\overset{N}{\underset{N}{|}}>C_{10}H_7\cdot NHEt$, is prepared in a manner similar to the preceding compound, 1:3:4-diamidotoluene being employed in place of diamidobenzene. It forms stellate groups of needles or golden-yellow plates, melts at 182°, and closely resembles the foregoing base, but is rather less soluble. The *hydrochloride* and *sulphate* form coppery needles, whilst the *nitrate* separates from alcohol in brownish-red needles with a bronze lustre. The *platinochloride* forms small, scarlet needles; the *aurochloride* a scarlet, microcrystalline powder; and the *acetyl* compound straw-yellow, prismatic crystals, sparingly soluble in almost all indifferent solvents.

α-Phenylamido-α-naphthatolazine,  $C_6H_3Me<\overset{N}{\underset{N}{|}}>C_{10}H_7\cdot NHPh$, is prepared from 1:3:4-diamidotoluene and benzeneazo-α-phenylnaphthylamine hydrochloride (Abstr., 1890, 908); it crystallises with some difficulty from alcohol in slender, brass-yellow needles, melts at 214°, and is sparingly soluble in most solvents. The solutions are reddish-yellow, and show a strong, yellowish-green fluorescence. The salts are likewise sparingly soluble, and have a Bordeaux-red colour in solution. The *hydrochloride* forms brownish-red needles with a metallic lustre, which are readily soluble in alcohol; and the *nitrate*, slender, brown needles with a bronze lustre, which are also fairly soluble in alcohol. The *platinochloride*, $C_{23}H_{17}N_3,H_2PtCl_6$, forms dark-red, microscopic needles, and the *aurochloride* a brownish-red, microcrystalline powder.

α-Dimethylamido-α-naphthaphenazine,  $C_6H_4<\overset{N}{\underset{N}{|}}>C_{10}H_7\cdot NMe_2$, is prepared from orthodiamidobenzene and benzeneazo-α-dimethylnaphthylamine; it crystallises from alcohol in slender, brownish-yellow needles, melts at 221°, is sparingly soluble in ether and light petroleum, more easily in benzene, toluene, and cold alcohol, forming yellowish-red solutions with a yellowish-green fluorescence. The base also sublimes in woolly needles, and is taken up by concentrated hydrochloric and sulphuric acids with a greenish-red colour, whilst the solution in acetic acid or dilute mineral acids is cherry-red. An isomeric compound has been described by Witt (Abstr., 1888, 491) as *dimethylnaphtha-eurhodine*, in which the dimethylamido-group is situated in the benzene nucleus. The *hydrochloride* of the new base forms garnet-red needles with a coppery lustre, whilst the *nitrate* crystallises from alcohol in bronze-coloured needles; the *sulphate* forms coppery needles, the *platinochoride* and *aurochloride* brownish-red needles.

α-Dimethylamido-α-naphthatolazine,  $C_6H_3Me<\overset{N}{\underset{N}{|}}>C_{10}H_7\cdot NMe_2$, crystallises best from boiling alcohol, and forms brownish-yellow needles melting at 230°. It closely resembles the foregoing base, but is rather less soluble, and sublimes with partial carbonisation in woolly needles; it dissolves in dilute mineral acids with a cherry-red colour, and in concentrated sulphuric acid with a green colour. The *hydrochloride* and *sulphate* form garnet-red needles with a coppery lustre, readily soluble in alcohol; the *nitrate* crystallises in slender, sparingly-soluble needles with a bronze lustre, and the *platinochloride* and *aurochloride* in brownish-red needles.

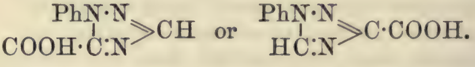
The formation of α-dimethylamido-α-naphthaphenazine and tolazine proves that the α-amido-α-naphthaphenazine prepared from them really contains the primary amido-group, as already maintained by Fischer and Hepp against Kehrmann (Abstr., 1890, 1266, 1444).

H. G. C.

Oxidation of Phenylmethyltriazolecarboxylic Acid; Phenyltriazoledicarboxylic Acid and the Constitution of α-Phenyltriazolecarboxylic Acid. By J. A. BLADIN (*Ber.*, **23**, 3785—3789).—In the author's previous communication (Abstr., 1890, 1165), the preparation of the acid potassium salt of phenyltriazoledicarboxylic acid by the oxidation of phenylmethyltriazolecarboxylic acid was described. All attempts to obtain the free acid have been without success, as it loses carbonic anhydride so readily, forming α-phenyltriazolecarboxylic acid. The salts also, with the exception of the normal potassium salt, and probably also the normal sodium salt, readily undergo the same decomposition when boiled. The *normal potassium salt* is extremely soluble in water, as are also the *calcium* and *barium* salts. The *potassium ammonium* salt, obtained by dissolving the acid potassium salt in ammonia and adding alcohol, is an amorphous, very soluble mass which is decomposed at 100°. The *silver* salt, $C_2N_3Ph(COOAg)_2 + \frac{1}{2}H_2O$ (?), is a white, amorphous, sparingly-soluble, voluminous precipitate which is partially decomposed at 100°; the water of crystallisation being evolved at 80°. The *copper* salt, $C_2N_3Ph(COO)_2Cu + 4H_2O$, is sparingly soluble in water, and crystallises in small, blue needles which lose their water at 100°, simultaneously undergoing further decomposition.

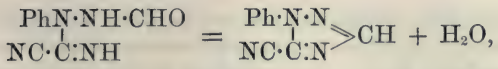
The *dimethyl* salt, $C_2N_3Ph(COOMe)_2$, is prepared by the action of methyl iodide on the silver salt; it crystallises from alcohol in hard, laminated crystals, or very slender, elastic needles, and melts without decomposition at 167°. The *diethyl* salt, $C_2N_3Ph(COOEt)_2$, crystallises from solution in a mixture of ether and light petroleum in slender, elastic needles melting at 81·5°.

From the above formation of α-phenyltriazolecarboxylic acid, it might have a constitution represented by either of the following formulæ:—



$$\begin{array}{r}\mathrm{PhN{\cdot}N}\\ \mathrm{COOH{\cdot}\overset{|}{C}{:}N}\end{array}\!>\mathrm{CH}\quad\text{or}\quad\begin{array}{r}\mathrm{PhN{\cdot}N}\\ \mathrm{H\overset{|}{C}{:}N}\end{array}\!>\mathrm{C{\cdot}COOH}.$$

In order to decide which of these is correct, the formyl compound of dicyanophenylhydrazine (Abstr., 1885, 980) was boiled with alcoholic potash, ammonia being given off. On adding water, evaporating off the alcohol, and adding hydrochloric acid, a brown, crystalline mass was obtained, which, on purification, was found to be identical with α-phenyltriazolecarboxylic acid. The condensation of formyldicyanophenylhydrazine in all probability takes place in the following manner:—



$$\begin{matrix}\text{PhN}\cdot\text{NH}\cdot\text{CHO}\\ |\\ \text{NC}\cdot\text{C:NH}\end{matrix} = \begin{matrix}\text{Ph}\cdot\text{N}\cdot\text{N}\\ |\\ \text{NC}\cdot\text{C:N}\end{matrix}\!\!>\text{CH} + H_2O,$$

the cyanogen group being then converted into carboxyl. The acid must therefore have the first of the formulæ given above.

H. G. C.

Nicotine. By A. Pinner and R. Wolffenstein (*Ber.*, **24**, 61—67).—When nicotine is mixed with platinum sponge and such a quantity of hydrogen dioxide that 3 atoms of active oxygen are present for each molecule of the base, and the whole allowed to remain for several weeks, the nicotine odour completely disappears. The liquid is then evaporated at 40—50° in a vacuum, and the pale-yellow syrup extracted with alcohol. After evaporating off the latter in a vacuum, and allowing the residue to remain in an exsiccator, it solidifies to a crystalline, deliquescent mass very soluble in water and alcohol, insoluble in ether. It is a base, most of the salts of which are syrups, but the *platinochloride* and *picrate* have been obtained in crystals. The former is prepared by adding platinic chloride to a mixture of the base with a little hydrochloric acid, allowing to remain for two days, and collecting the granular, crystalline, orange-red salt. This is soluble in hydrochloric acid, is reprecipitated by soda with partial decomposition, and has the composition $C_{10}H_{12}N_2O,H_2PtCl_6$. The *picrate*, $C_{10}H_{12}N_2O,2C_6H_3N_3O_7$, is formed by adding an excess of a saturated solution of picric acid to an aqueous solution of the base, and forms slender, seemingly rhombic needles melting at 154—158°. The base has, therefore, the composition $C_{10}H_{12}N_2O$, being formed from nicotine by the substitution of one atom of oxygen for two atoms of hydrogen, and may be termed for the present *oxynicotine*. It is not volatile in a current of steam, is scarcely acted on by aqueous potash, and has physiological properties resembling, but much feebler than, those of nicotine. On oxidation with potassium permanganate, it is converted into nicotinic acid.

Attempts were made to obtain evidence of the presence of imido-groups in nicotine by treating it with nitrous acid, acetic anhydride, and benzoic chloride in alkaline solution, but without any definite result. Acetic anhydride does act on nicotine at 150—170°, but the nature of the product is not yet ascertained. Benzoic chloride in alkaline solution does not act on the nicotine, but is simply converted into benzoic anhydride. By the action of benzoic chloride on the base itself at the ordinary temperature or at 100°, a product is formed which, however, does not seem to be a benzoyl derivative of nicotine, and is not identical with the additive product of 2 mols. of benzoic chloride and nicotine obtained by Will (*Annalen*, **118**, 206). These products are being further investigated. H. G. C.

Solanidine of Potato Sprouts. By A. Jorissen and L. Grosjean (*Chem. Centr.*, 1890, ii, 788; from *Bull. Acad. Belg.* [3], **19**, 245).—By extracting the young sprouts of potatoes with ether, recrystallising the residue of the ether extract from alcohol, dissolving in a mineral acid, precipitating with alkali, and finally recrystallising from ether, a substance is obtained which is identical with the solanidine obtained from solanine. It crystallises in long, white, silky needles, is nearly insoluble in water, soluble in alcohol, very soluble in ether, and melts at 208°. It is alkaline to litmus, has a sharp, bitter taste, and combines with acids to form salts. If the solution of the base in acetic acid be concentrated on the water-bath, concentrated hydrochloric acid and a little ferric chloride added, and the mixture then evaporated to dryness, a violet coloration is produced. About 1·5 grams of the base is obtained from 100 grams of the fresh sprouts. J. W. L.

Metallic Derivatives of Cupreïne. By A. C. OUDEMANS, Jun. (*Rec. Trav. Chim.*, **9**, 171—183).—The sodium and potassium compounds of cupreïne separate as crystalline scales when a solution of the alkaloïd in slight excess of the corresponding hydroxide is subjected to cold. The separated scales are dried by a filter pump, washed rapidly with strong alcohol, and placed in a desiccator over potassium hydroxide for some time. *Potassium cupreïne*, $C_{19}H_{21}KN_2O_2 + 8H_2O$, forms acicular crystals or hexagonal scales. *Sodium cupreïne*, $C_{19}H_{21}NaN_2O_2 + 5H_2O$ and $+ 8H_2O$, forms large scales which are greasy to the touch. The potassium compound appears to be more soluble in mixtures of aqueous and alcoholic alkalis than the sodium derivative.

In contradistinction to Hesse, who denied the existence of an ammonium derivative of cupreïne, the author states that the alkaloïd dissolves easily in concentrated ammonia solution, to a smaller extent in weaker solutions, and inasmuch as the specific rotatory power of such solutions is similar to that of like solutions of the sodium derivative, he concludes that an ammonium compound does exist. Solutions of lithium hydroxide and of barium hydroxides also dissolve cupreïne. All the metallic derivatives of cupreïne assume an orange or brick-red colour after prolonged drying or on heating above 120°.

Hesse having proved that cupreïne behaved as a phenol in which hydrogen may be displaced by a metal, the author has investigated the influence such replacement has on the specific rotatory power of the alkaloïd, in order to determine if the alkaloïd and the base combined molecule for molecule, in which case an excess of base ought not to affect the specific rotatory power to any great extent, and he publishes very complete tables of the specific rotatory power of the alkaloïd in both aqueous and alcoholic solutions of potassium and sodium hydroxides, in aqueous solutions of lithium and barium hydroxides, and in ammonia solution.

The results of the observations are as follows:—1. Approximately the same values obtain for the sp. rot. power of cupreïne for similar concentrations of alkaloïd and either potassium, sodium, lithium, and barium hydroxides in aqueous solution, but in the case of the ammoniacal solution the rotatory power has a higher value, and differs in the values obtained from its solution in fixed alkalis in the fact that an increased strength of ammonia solution augments the sp. rot. power. 2. The sp. rot. power of the alkaloïd diminishes inversely with the amount present in the alkaline solution, and also with the amoun of alkaline hydroxide present. 3. The highest values for the sp. rot.

power are obtained when the amounts of alkaloïd and of hydroxide associated are approximately those represented by their molecular weights; in this respect cupreïne is analogous to quinamine and conquinamine in acid solution. It is to be noted that the values obtained in alkaline alcoholic solution are much higher than those in aqueous solution, and that in this case additional alkali increases the rotatory values.

The mean rotatory power for 1 mol. (in milligrams) of cupreïne in 20 c.c. of water with 1—2 mols. (in milligrams) of alkaline hydroxide is about −205°. T. G. N.

Dextrococaïnes. By A. DECKERS and A. EINHORN (*Ber.*, **24**, 7—12; compare Abstr., 1890, 649, 913).—By the action of cinnamic chloride on methyldextroecgonine at 150—160°, the latter is converted into *methylcinnamyldextroecgonine*,

$$C_5NH_7Me{\cdot}CH(O{\cdot}CO{\cdot}CH{:}CHPh){\cdot}CH_2{\cdot}COOMe.$$

When the product is poured into water, some cinnamic acid is precipitated; the filtrate is made alkaline with potassium carbonate, and the alkaloïd extracted with ether and purified by conversion into the hydrochloride. When precipitated from the latter, it forms an almost colourless oil which soon solidifies to long, radially grouped prisms melting at 68°. A 2·11 per cent. alcoholic solution in a 200 mm. tube rotates the plane of polarisation +2°. The *hydrochloride*,

$$C_{19}H_{23}NO_4,HCl,$$

crystallises from hot water in white needles melting at 186—188°; the *platinochloride*, $(C_{19}H_{23}NO_4)_2,H_2PtCl_6$, from alcohol in small, pale-yellow needles melting at 208—210°; and the *aurochloride*, $C_{19}H_{23}NO_4,HAuCl_4$, in orange needles melting at 164°. The *hydrobromide*, $C_{19}H_{23}NO_4,HBr$, forms small needles melting at 209°, and the *nitrate*, $C_{19}H_{23}NO_4,HNO_3$, beautiful, long needles melting at 197°.

Cinnamyldextroecgonine,

$$C_5NH_7Me{\cdot}CH(O{\cdot}CO{\cdot}CH{:}CHPh){\cdot}CH_2{\cdot}COOH,$$

is prepared by the action of cinnamic chloride or anhydride on dextroecgonine, and forms an oil which only solidifies after a long time, and then crystallises from hot water in badly-developed crystals. The *hydrochloride*, $C_{18}H_{21}NO_4,HCl$, crystallises in white needles which darken at 228° and melt with decomposition at 236°, whilst the *platinochloride* forms pale-yellow needles which melt with decomposition at 223°.

Methylisovaleryldextroecgonine,

$$C_5NH_7Me{\cdot}CH(O{\cdot}CO{\cdot}C_4H_9){\cdot}CH_2{\cdot}COOMe,$$

is prepared in the same way from isovaleric chloride and methyldextroecgonine at 112—114°, and forms a transparent oil, a 2·01 per cent. solution of which rotates the plane of polarisation +1·02° in a 200 mm. tube. The *hydrochloride*, $C_{15}H_{25}NO_4,HCl$, and the *nitrate*, $C_{15}H_{25}NO_4,HNO_3$, form small, nacreous plates melting at 192° and 163° respectively; the *platinochloride*, $(C_{15}H_{25}NO_4)_2,H_2PtCl_6$, crystallises in lemon-yellow needles melting at 202°, and the *aurochloride* in pale-yellow needles melting at 88°. *Isovaleryldextroecgonine*, $C_{14}H_{23}NO_4$, obtained by acting on dextroecgonine with isovaleric chloride, and treating the hydrochloride thus formed with silver oxide, crystallises from a mixture of methyl alcohol and ether in small needles melting at 224° with decomposition. The *hydrochloride*, $C_{14}H_{23}NO_4.HCl$, forms small, lustrous needles which darken at 206° and melt at 236°; the *platinochloride*, $(C_{14}H_{23}NO_4)_2,H_2PtCl_6$, crystallises in orange prisms melting at 216°.

Dimethylorthophthalyldidextroecgonine,

$$C_6H_4:C_2O_2[O\,CH(C_5NMeH_7)\cdot CH_2\cdot COOMe]_2,$$

is formed by heating equal weights of orthophthalic chloride and methyldextroecgonine at 150—160°. It is a reddish oil, and forms salts, of which only the *hydriodide*, $C_{28}H_{36}N_2O_8,2HI$, has been obtained crystalline. *Orthophthalyldidextroecgonine*, $C_{26}H_{32}N_2O_8$, prepared from dextroecgonine by the action of phthalic anhydride, is also an oil; its *hydriodide*, $C_{26}H_{32}N_2O_8,2HI$, forms yellowish, badly-developed crystals melting at 103°. H. G. C.

Ptomaïnes formed in the Cultivation of the Swine Fever Bacillus. By E. A. v. SCHWEINITZ (*Chem. Centr.*, 1890, ii, 759—760; from *Med. News*, September 6th, 1890).—The bacillus of swine fever was cultivated in peptone broth at 37°. The broth was afterwards acidified with hydrochloric acid, concentrated on the water-bath, the residue extracted with 98 per cent. alcohol, and the extract precipitated with mercuric chloride solution. The precipitate, suspended in water, was treated with hydrogen sulphide, and in the filtrate cadaverine, a primary amine of unknown composition, and an alkaloïd, the platinochloride of which had the formula $C_{14}H_{34}N_2PtCl_6$, were found. The free base could not be isolated; the hydrochloride forms a syrup soluble in alcohol. If the broth containing the bacillus cultivation be treated with excess of alcohol, an amorphous precipitate is formed which dissolves in water. By repeatedly precipitating this and redissolving it several times, an albumose is separated which may be obtained in a crystalline form by concentrating in a vacuum over sulphuric acid. Neither this nor the above-mentioned base has poisonous properties.

By treating the broth, after cultivation, in the manner described by Brieger and Fränkel, an albumose of properties corresponding with the toxalbumoses is obtained, which also is without poisonous properties when subcutaneously injected into the guinea pig.

J. W. L.

Egg Albumin free from Ash. By E. HARNACK (*Ber.*, **23**, 3745—3752, compare Abstr., 1890, 272).—The author gives further details of the method employed for the preparation of pure albumin free from ash by treatment of the copper derivative with concentrated potash. The albumin so obtained is soluble in boiling water; the addition of alcohol causes no change, but neutral salts immediately produce a flocculent precipitate. On heating the moist preparation under water, it melts before dissolving. Ammonium sulphate yields a crystalline albumin derivative, which, however, only contains about 5 per cent. of albumin.

Albumin reddens blue litmus-paper, and is not precipitated from solution by many organic acids, such as formic acid, acetic acid, tartaric acid, citric acid, or lactic acid. The precipitate caused by most mineral acids consists of unaltered albumin, as is proved by the fact that after filtration and washing it is soluble in water.

Alkalis prevent the precipitation of albumin by neutral salts.

Free albumin, even in presence of moisture, shows no tendency to ferment or decay.

The paper closes with a discussion of the part played by albumin in the animal economy. J. B. T.

Compound of Gelatin and Metaphosphoric Acid. By R. Lorenz (*Pflüger's Archiv*, **47**, 189—195).—It was thought interesting to investigate the proportion of metaphosphoric acid in the precipitate produced by adding that acid to solutions of gelatin, in view of recent researches by Krüger on the relation of gelatin to bases. There was some difficulty in obtaining a precipitate which could be readily collected and washed, especially with β-gelatin, that is, gelatin which has been rendered non-gelatinisable by prolonged boiling. In three different preparations of ordinary gelatin (gelatin α), the percentage of phosphoric anhydride was respectively 7·5, 5·3, and 6·1. It was found that this was probably due to the length of time during which the washing was continued; prolonged washing with water dissolving out more and more phosphoric acid. The same preparation was analysed at intervals with the following results:—

After	2	days' washing,	7·1	per cent. of	P_2O_5.
,,	10	,,	6·4	,,	,,
,,	22	,,	5·8	,,	,,
,,	35	,,	4·5	,,	,,

Estimation of the phosphoric anhydride in two preparations made from β-gelatin gave respectively 6·9 and 8·35 per cent.

W. D. H.

Metaphosphoric Acid in the Nucleïn of Yeast. By L. Liebermann (*Pflüger's Archiv*, **47**, 155—160).—The author has previously stated (Abstr., 1888, 510, 1889, 1021) that metaphosphoric acid can be separated from nucleïn; the present paper relates to the preparation of the barium salt of the acid from acid extracts of yeast nucleïn.

The following results of elementary analyses of three preparations, are considered sufficiently near to the percentages calculated from the formula to support the author's previous contention.

	I.	II.	III.	By calculation.
Ba	38·61	37·33	40·73	46·44
PO_3	53·26	58·11	59·25	53·56

W. D. H.

Action of Hydrofluoric Acid on Diastase. By J. Effront (*Bull. Soc. Chim.* [3], **4**, 627—632).—Hydrofluoric acid in amounts varying from 5—10 milligrams per 100 c.c. of malt infusion exercises a marked influence in the conservation of the diastatic properties of the infusion, and this is probably due to the retarding influence of the acid on the development of the lactic and butyric fermentations which cause coagulation of the diastase (see p. 488).

In presence of these small quantities of hydrofluoric acid, the degree to which the hydrolysis of starch paste by malt infusion can be carried is augmented, and the most favourable temperature for such is 30°.

Similar results obtain in the case of worts derived from raw grain. Numerous experimental data are given. T. G. N.

Myohæmatin. By S. M. Copeman (*Proc. Physiol. Soc.*, 1890, 22).—By treating defibrinated and slightly diluted blood with a small quantity of minced muscular tissue, and subsequently keeping the mixture at 38° for nearly three weeks contact with the air being prevented, a form of myohæmatin is produced of which the spectrum resembles that figured by MacMunn, except for a slight difference in shading of the band nearest the violet. It is easily distinguishable from hæmochromogen and hæmatoporphyrin. On heating to near the boiling point, the bands disappear, becoming visible again on cooling, as observed in the case of MacMunn's modified myohæmatin.

Similar experiments carried out with small quantities of hepatic and other tissues macerated in blood resulted in the formation of alkaline hæmatin only, instead of a form of histo-hæmatin.

W. D. H.

Physiological Chemistry.

In what Form is Iron Absorbed? By C. A. Socin (*Zeit. physiol. Chem.*, **15**, 93—139).—Experiments were performed in three cases on dogs; the iron contained in yolk of egg, the food selected, was estimated; the fæces and urine were then examined for iron, and the amount found there in two out of the three cases was much greater than in the food. From these experiments, the conclusion is drawn that a simple comparison of the amounts of iron ingested and excreted affords no trustworthy data in the solution of questions relating to the metabolism of iron.

Mice were then selected as the animals on which the remaining experiments were performed. They lived normally when fed on yolk of egg, from which the conclusion is drawn that the organic iron-containing compounds (hæmatogen) in that article of diet are assimilable; this was supported by the fact that the iron excreted was less than that ingested. Mice fed on artificial diets constructed of iron-free proteïds, carbohydrates, and fat soon died; but they died equally soon if inorganic or organic compounds of iron were mixed with this diet.

From this, the conclusion is drawn, that a life-sustaining artificial diet, although apparently containing all that is necessary, cannot yet be constructed.

Among other conclusions arrived at are the following:—Filtered urine of animals fed on normal diet contains only traces of iron; serum albumin prepared from hæmoglobin-free serum contains no iron.

W. D. H.

Influence of Muscular Work on Proteïd Metabolism. By O. KRUMMACHER (*Pflüger's Archiv*, **47**, 454—468).—Argutinsky (this vol. p. 350) found that excessive muscular work produced in himself an increase in the output of nitrogen, derived presumably from an increase in the destructive metabolism of the proteïds of the body. In case this should have been due to an idiosyncrasy, it was deemed necessary to repeat the experiments. The present paper is an account of such an experiment carried out on the author's own person; full details are given. The general conclusion is the same as that of Argutinsky.

W. D. H.

Fate of Morphine in the Animal Organism. By E. TAUBER (*Chem. Centr.*, 1890, ii, 666—667; from *Arch. experim. Path. Pharm.*, **27**, 335).—Since the researches into the change or otherwise which morphine undergoes in the animal organism, which have been undertaken by different workers, have led to contradictory results, the author has both added the alkaloïd to blood directly, and has injected it subcutaneously into a dog. From the blood, 95 per cent. of the alkaloïd was recovered by the following method:—The blood was coagulated by the addition of acetic acid, and the coagulum washed with acidified water until colourless. The filtrate was then precipitated with lead acetate, the precipitate washed with water followed by alcohol, the alcohol distilled off, the lead precipitated as sulphide, the filtrate evaporated, the residue extracted with alcohol, the alcohol again distilled off, and the residue extracted with a little water. From this solution, the morphine is precipitated with sodium hydrogen carbonate. An allowance of 1 milligram must be made for the morphine which remains in solution. In another experiment, 1·6 grams of morphine hydrochloride was subcutaneously injected into a dog during ten days, after which 0·512 gram of morphine was found in the fæces.

J. W. L.

Fate of Peptone. By L. E. SHORE (*J. Physiol.*, **11**, 528—560).—There is no doubt that peptone absorbed from the alimentary canal undergoes during the process of absorption a reconversion into ordinary proteïds. Hofmeister (*Zeit. physiol. Chem.*, **5**) considered that the leucocytes of adenoid tissue and of the blood, but more especially of the lymph, had the power of effecting this change. Heidenhain (*Pflüger's Archiv*, **43**, Supplemental No.) showed, however, that the amount of and percentage of proteïd in chyle will not account for the large quantities of proteïd absorbed, and he calculated that if the transformation were effected by leucocytes, 20 grams of dry cell substance would have to fix and transform 274 grams of dry proteïd (compare Neumeister, this vol., p. 233). In the present research, the questions especially investigated were the fate of peptone when introduced directly into the lymphatic channels, and by experiments on lymphatic glands, whether lymph cells can assimilate peptone or not. The word peptone as used here includes the small admixture of albumoses present in the preparation used (Grübler's). The method of detecting peptone was with slight modifications that already used by Neumeister. The animals used were dogs. It was found that peptone, when injected into the blood stream, rapidly reappears in the urine, but that when the renal vessels are ligatured, it disappears from the blood, and passes into (is secreted into, Heidenhain) the lymph. When peptone is injected into the ligatured bile-duct, it also reappears in great measure in the lymph; some of it, however, passes into the blood, and finally (with a small amount of bile pigment) into the urine. From the lymph in the tissues, the peptone is gradually carried to the thoracic duct, and then enters the blood again. In this course it must enter lymphatic glands, and as a large percentage is ultimately recoverable in the urine, it suffers little or no transformation by the lymphatic leucocytes. When peptone (in these experiments dissolved in the lymph serum obtained from the thoracic duct of the same animal) is injected directly into a lymphatic vessel in the lower limbs, it is for a time recoverable as such in the lymph of the thoracic duct. This lymph must have passed through lymphatic glands; in fact, the anatomical relation of these glands to the vessels was accurately determined by injection of sodium sulphindigotate. The cells of lymphatic glands have, therefore, not the power of assimilating peptone. It was also found that the cells of the liver and spleen take no part in the transformation of peptone. The general conclusion is therefore drawn that this is normally brought about by the epithelial cells of the mucous membrane of the alimentary canal. Heidenhain, under whose superintendence this work was done, believes that five minutes is the length of time necessary for the passage of fluid through these cells, and that this is sufficient for the accomplishment of the transformation.

W. D. H.

Cutaneous Pigment as an Antecedent of Hæmoglobin. By S. Delépine (*Proc. Physiol. Soc.*, 1890, 27—34).—Although chlorophyll and hæmoglobin bear so many resemblances to one another, light is an essential factor in the production of the former, but as red blood corpuscles are formed in parts of the body not exposed to light, it would seem not to be so in that of the latter. The influence of sunlight in the production of melanin in the epidermis afforded at one time no key to the explanation of this difference, as melanin, like other animal pigments, was considered to have its origin in hæmoglobin.

It having been shown, however, that hæmoglobin is decomposed in the liver, the iron being retained by the liver cells, and probably used for the formation of new hæmoglobin, attention was directed to the way in which the rest of the pigment was reproduced. The examination of melanotic tumours gave a clue to the question, and the facts collected in support of the view that melanin (formed in the skin under the influence of light) is the precursor of hæmoglobin, are the following:—

Although the production of melanin is often increased in the skin under the influence of certain stimuli, it gradually disappears when these stimuli cease to act. It must be transformed into some colourless product, which must pass either towards the surface or into the deeper tissues. Instances of such stimuli are luminous heat (sunburn), chemical irritants (mustard poultices), mechanical stimuli (scratching), pregnancy, certain pathological states, &c. The pigment deposited is in the *deep* layers of the *rete Malpighi*. Melanin is never produced when the epidermis is absent. The pigment can, moreover, be traced to the lymphatics in the true skin.

There are certain conditions in which the formation of melanin is lessened; absence of heat and light; when the skin is inactive, or atrophied, as over scars, or its nerves divided or diseased as in the patches of leprosy, and in the complex state of things present in albinism. Imperfect production of cutaneous pigment is, moreover, often, if not always, associated with diminution in the hæmoglobin of the blood.

The following facts show that melanin is developed not from hæmoglobin, but independently of it:—(1) Melanin appears in many embryonic parts before any blood is formed. (2) In the adult, parts removed from all blood vessels, such as the crystalline lens, may become deeply pigmented. (3) The amount of melanin in the skin is not proportional to the amount of blood circulating through or extravasated into the subjacent tissues. The conclusion is therefore drawn that melanin is elaborated in certain epithelial cells, like products of glandular activity out of lymph, and is not a derivative of hæmoglobin.

The next series of facts deal with the fate of melanin. When the skin is deeply pigmented as in negros, some, but a very small portion, of the melanin passes into the superficial layers of the epidermis, and so reaches the surface. The greater part of the pigment, as is well seen in pathological specimens, passes into the lymphatics of the *cutis vera*, in some cases so much so as to partially obstruct them. Other forms of obstruction, as the pressure of tumours, will cause similarly a natural injection of the lymphatics with melanin. Under normal circumstances, however, this is not visible, as the melanin seems to be dissolved, and is absorbed and removed in a colourless form. This may be constant or intermittent; the most important conclusion arrived at, however, is that ultimately it is used in the formation of new hæmoglobin. The production of pigment in the skin should be limited by the accumulation of precipitated melanin in the *rete*. Such accumulation, as in negros, diminishes the intensity of the light reaching the deepest and most active parts of the epidermis, and therefore regulates the amount of normal stimulus acting on the cells.

W. D. H.

Effect of Peptone on the Clotting of Blood and Lymph. By L. E. Shore (*J. Physiol.*, **11**, 561—565).—After rapid injection of peptone into the blood, that fluid, and also the lymph, if withdrawn within an hour after the injection, do not clot (Schmidt-Mulheim, Fano). In the present research, it was found that slow injection of peptone into the blood does not prevent, or only very slightly, its coagulation when withdrawn, but that the lymph has no tendency to clot.

In experiments made with lymph out of the body, it was found that the addition of considerable quantities of peptone solution had no anti-clotting power, but that the addition of mere traces of peptone to the lymph prevented its coagulation. W. D. H.

Action of Leech Extract on Blood. By W. L. Dickinson (*J. Physiol.*, **11**, 566—572).—The general properties of the extract of the anterior part of the medicinal leech which as Haycraft showed (*Proc. Roy. Soc.*, **36**) possesses a strong anti-clotting action on blood are the following:—It is neutral to litmus paper; its specific gravity is not appreciably higher than that of the medium used for extraction. Boiling causes no precipitate, and no loss of activity. Alkalis cause no precipitate. A trace of acetic acid causes cloudiness readily soluble in excess. Strong acetic acid causes no precipitate in salt-free, but a copious cloud in salt-saturated, extracts. Nitric acid in the cold causes a precipitate soluble on boiling, and reappearing on cooling. Saturation with ammonium sulphate causes a precipitate, after which no proteïd remains in solution; saturation with magnesium sulphate or sodium chloride, on the other hand, causes no precipitate. If all salts are removed from the extract by dialysis, there is no precipitate produced, and no loss of power. Copper sulphate, lead acetate, and mercuric chloride give precipitates insoluble in excess of the reagents. Copper sulphate and potash give a pink (biuret) reaction. Alcohol causes no loss of the activity of the extract.

The leech extract, therefore, contains a proteïd having some features in common with Kühne's proto-, and others with deutero-albumose. The albumose precipitated by ammonium sulphate has all the anti-clotting power of the original extract; the extract *minus* the albumose has no such powers. Hence, probably the albumose is itself the active principle.

Clotting in plasma obtained from blood, prevented from coagulating by admixture with leech extract (either intravenously or after it is shed), cannot be induced by carbonic anhydride or by dilute acetic acid; it can, however, always be induced by a sufficient quantity of fibrin ferment. Such plasma gives no precipitate on cooling.

Fibrin soaked in leech extract fails to yield ferment when subsequently treated with 8 per cent. sodium chloride solution. The extract, however, still contains cell-globulin. Cell-globulin prepared from lymphatic glands by Halliburton's method (Abstr., 1888, 974) retains all its properties, except its fibrinoplastic power, when treated with leech extract. This is regarded as an argument in favour of the non-identity of the cell-globulin and fibrin ferment. W. D. H.

Transformation of Hæmoglobin in the Bile. By W. Filehne (*Chem. Centr.*, 1890, ii, 790; from *Arch. Path. Anat.*, **121**, 605).—In view of the researches of Wertheimer and Meyer (Abstr., 1889, 636), the author was led to repeat some experiments previously undertaken by him, but these were now made on the living animal instead of immediately after death. The earlier experiments with phosphorus,

arsenic, antifebrin, and glycerol were repeated, and hæmoglobin was again found in the bile of rabbits and dogs, although not in large quantity.
J. W. L.

Excretion of the Digestive Ferments from the Animal. By J. Benderski (*Chem. Centr.*, 1890, ii, 791; from *Arch. Path. Anat.*, **121**, 554—597).—The author has determined that a substance is always present in normal urine which dissolves fibrin in presence of an acid, and that it is destroyed at a boiling heat. The quantity varies considerably with different persons when in health, and consequently the variation in the amount of this substance in illness cannot have any importance, at least for diagnostic purposes. The author names it *uropepsin*. The presence of pepsin in urine must not therefore be considered indicative of the excretion of peptone by the animal, but of the formation of uropepsin in the urine.

In healthy urine, a trypsin is found which varies in quantity, and may be increased, or altogether wanting, in cases of disease. The author does not consider it identical with the pancreatic ferment. It differs from the latter in that it is not destroyed by boiling. It has been named *urotrypsin*.

An amylolytic ferment occurring in urine, and which is similar to, but not identical with, the ferment ptyalin, has been named *uroptyalin* by the author.

In animal sweat, another ferment occurs which behaves like uroptyalin with starch, and is named *hidroptyalin* by the author; it is an altered ptyalin.

Trypsin was not found in sweat, but a pepsin was observed which had an activity intermediate between that of pepsin and uropepsin.
J. W. L.

Excretion of Uric Acid and Nitrogen in cases of Leucæmia. By C. Bohland and H. Schurz (*Pflüger's Archiv*, **47**, 469—509).—Three cases of leucæmia are described with clinical details; most attention was devoted, however, to an examination of the urine and a comparison of the excretion of uric acid and of nitrogen with that of normal individuals on the same diet. An absolute increase of the output of uric acid was seen in all three, but more especially in two of the cases. Pott gives the relation of uric acid nitrogen to total nitrogen in health as 1 to 19·7. In the three cases of leucæmia, the proportion was respectively 1 to 9·4, 1 to 12·8, and 1 to 24·4. In this last case, there was a good deal of fever which no doubt produced a greater proportional output of total nitrogen than of uric acid.

The following are the mean numbers obtained:—

	Total nitrogen.	Uric acid.	Proportion of uric acid nitrogen to total nitrogen.
Normal......	—	0·65 grams	1 : 19·7
Case 1	13·1 grams	1·5 ,,	1 : 9·4
,, 2	8·7 ,,	0·68 ,,	1 : 12·8
,, 3	14·5 ,,	1·8 ,,	1 : 24·4

W. D. H.

Calcium Salts in Urine. By G. Hoppe-Seyler (*Zeit. physiol. Chem.*, **15**, 161—178).—A large number of observations on the quantity of calcium salts in the urine of numerous hospital patients are recorded. The special point investigated is the influence of rest and muscular movement on the amount of these salts in the urine. It was found that rest in bed produces a great increase in the output of these salts. This is especially noticeable in children and young people. On these rising from bed and resuming activity, the output sinks to the normal, which is stated by Neubauer (*J. pr. Chem.*, **67**, 65) to be 0·33 gram of calcium phosphate per diem.

Neubauer's method of estimation was used in the present analyses. Reckoned as calcium phosphate, the daily output in those lying in bed was found to average 0·721, while in those who were not confined to bed it was 0·37 gram. An exception to this occurs in febrile disorders, where there is a diminished excretion of calcium salts; this is doubtless in part dependent on the small amount of food taken. Injection of calomel in syphilitic patients was found to lead to an increased output of calcium salts in the urine. W. D. H.

Urine and Blood in a Case of Melanotic Sarcoma. By F. Hoppe-Seyler (*Zeit. physiol. Chem.*, **15**, 179—188).—The case of melanotic tumour from which specimens of blood and urine were obtained was a hæmorrhagic one, and thus fairly large quantities of blood were collected.

Analysis of the blood, performed in the usual way, gave the following results:—

1000 parts of blood yielded 320·99 parts of red corpuscles, and 679·01 parts of plasma.

The composition of red corpuscles and serum may be stated in a table as follows:—

	Red corpuscles.	Serum.
Oxyhæmoglobin	404·06	—
Proteïds	0·81	67·68
Lecithin	1·62	2·323
Cholesterol	5·70	0·654
Fat	—	3·473
Alcoholic extract	1·59	1·63
Aqueous extract	7·72	2·18
Solid organic matters	423·41	77·94
Water	576·59	914·53
Inorganic salts		7·53
	1000·00	1000·00

Special attention is directed to the low percentage of water (as compared with other mammals and other tissues), of lecithin and of proteïd matter (other than hæmoglobin) in the red corpuscles. Nothing noteworthy, from a pathological standpoint, was, however, noted in the blood.

In connection with the urine, special attention was directed to the pigment which gave the urine a dark-brown colour darkening on exposure, or on heating with nitric acid. It was found to consist of urobilin in small quantities, and a second pigment which is very soluble; the latter is precipitable by normal lead acetate, and on fusing with alkali gives off ammonia, whilst a residue of humic acid and protocatechuic acid remains behind. It therefore somewhat resembles a humous substance. Indole was also formed as a result of fusion with alkali; proteïd was, however, not present in the urine.

W. D. H.

Action of Poisons on Nerve-fibres and Peripheral Nerve-cells. By J. N. Langley and W. L. Dickinson (*J. Physiol.*, **11**, 509—527).—The superior cervical ganglion of an anæsthetised rabbit was exposed, and a 1 per cent. solution of the poison was applied to it locally, or the drug was injected subcutaneously. The effect of stimulation of the sympathetic nerve, on each side of the ganglion, on the size of the pupil and blood vessels was then observed. Those substances which have no effect are atropine, hyoscine, eserine, muscarine, pilocarpine, picrotoxin, caffeïne, and antipyrine. Those substances, local application of which annuls more or less readily the irritability of nerve-fibres, but injection of which has little or no effect, are codeïne, apomorphine, aconitine, and cocaïne. Those substances which on injection into the blood, or applied locally, have a more or less paralysing action on the ganglion are coniine, curarine, brucine, and strychnine. The pupillo-dilatator nerve-cells are paralysed far more readily than the vaso-constrictor nerve-cells. The authors have previously shown that the action of nicotine is similar.

W. D. H.

Action of Nicotine on Invertebrates. By M. Greenwood (*J. Physiol.*, **11**, 573—605).—The authoress thus summarises her own observations:—

The toxic effect of nicotine on any organism is determined mainly by the degree of development of the nervous system. Thus for *Amœba* or *Actinosphærium* it cannot be regarded as exciting or paralysing; it is rather inimical to continued healthy life. As soon as any structural complexity is reached, the action of the drug is discriminating in such a fashion that the nervous actions which are the expressions of automatism, which imply co-ordination of impulse, are stopped first. This is seen dimly in *Hydra*, and it is more pronounced among the *Medusæ*, where spontaneity, irradiation of impulse, and direct motor activity are affected successively. When structural devolopment goes further, the selective action is traced readily, as in *Antedon*. In the case of the higher invertebrates, the paralysing action of nicotine is preceded by a phase of stimulation. This becomes marked in *Ophiurids* and *Crinoids*. As this positively-exciting action becomes noticeable, nicotine becomes more and more a medium in which life is impossible. Thus *Amœba* is not killed at once by a 1 per cent. solution of nicotine tartrate; *Hydra* dies speedily in such concentration, but will live over night in 0·05 per cent., while *Lumbricus* is killed by this strength, but lives for some hours in a 0·01 per cent. solution.

When very simple animals (*Actinosphærium*, *Hydra*, *Medusæ*) die under the influence of nicotine, death is often associated with injury of their substance, so that it tends to disintegrate; and the definite poisoning that occurs in higher types has sometimes, as one of its after-effects, a lingering trophic disturbance. An extreme form of this is seen in *Palæmon*, where there may be actually a progressive death of tissues from behind forwards. Similar lesions find expression in the growth of fungus on a paralysed *Crayfish*, and in the clinging of earth particles to the body of a poisoned *Earthworm*. Though nicotine acts on any organism according as the nervous system is or is not developed, closely allied animals may yet react differently, according to their individual balance of organisation.

W. D. H.

Effect of Morphine on Cats. By L. GUINARD (*Compt. rend.*, **111**, 981—983).—When morphine is administered to cats by hypodermic or intravenous injection, in doses varying from 0·0004 gram to 0·09 gram per kilo. of body weight, it never produces sleep or narcotic prostration. On the contrary, it produces a remarkable degree of excitement, increasing in intensity with the dose given. This excitement is accompanied by evident disorder in the functions of the brain, and if the dose is large, terminates in a period of convulsions, ending in the death of the animal.

Milne-Edwards (p. 983) has been unable to obtain narcotism by administration of morphine to cats either by ingestion with food or by injection. He has also found that lions and tigers offer a similar resistance to the narcotising influence of the alkaloïd. C. H. B.

Action of Strychnine. By K. SCHLICK (*Pflüger's Archiv*, **47**, 171—189).—Whilst mechanical, thermal, and electrical stimulation of a strychnine-poisoned frog produce a marked increase in the reflex responses, chemical stimuli do not produce this result. A chemical stimulus, which is very active before the injection of the alkaloïd, produces little or no effect on the poisoned animal. Under all conditions, the reflex time is lengthened by strychnine. W. D. H.

Physiological Action of Cocaïne. By U. MOSSO (*Pflüger's Archiv*, **47**, 553—601).—Cocaïne applied locally to a motor nerve paralyses it; it also acts injuriously on the nerve-cells of the spinal cord. It has been supposed that cocaïne acts on the sensory nerves, as curare does on the motor nerves, but the present experiments do not entirely support this view; cocaïne has no specific action, but its effects are similar to those produced by the application of cold to the nervous system.

In an animal in which a large part of the spinal cord remains intact while the rest is poisoned with cocaïne, sensibility is lost after motility; cocaïne, therefore, arrests the outgoing impulses from the cord.

Regarding doses, the following are the numbers obtained from experiments on dogs:—0·0005 gram per kilo. of body weight produces no action on the muscles; 0·001 gram produces increased contraction; 0·003 gram acts in the opposite way. This action of the drug on the motor apparatus seems to have been missed by previous observers, because attention has been, as with other anæsthetics, more particularly directed to its influence on sensibility; the great advantage of cocaïne as an anæsthetic appears to be the fact that it is completely destroyed in the organism; its effects soon pass off, and leave no bad after-effects.

Experiments on human beings gave the following results:—Doses of 0·1 gram given by the stomach increase the capacity for muscular work; if it is injected into the blood stream, there is first increased then lessened excitability of the motor apparatus as in animals. The beneficial action of cocaïne is even greater when the muscles have been previously fatigued, or the individual has been fasting; in the latter case the work may be as much as doubled. This was tested graphically by recording the contraction of the fingers, the muscles of which were stimulated electrically; after a long march, fatigue does not ensue so readily with as without cocaïne. Small doses (0·05 gram to 0·1 gram given by the mouth) increase the sensibility of the skin, and shorten the reaction time. The drug increases the quantity of air inspired, even though the frequency of respiration does not rise, as it, however, generally does; small doses cause marked contraction of the blood vessels.

It increases the body temperature in frogs. Very small doses increase, larger ones abolish, the patella tendon reflex. The intensity of the action of cocaïne differs in different classes of vertebrates. In plants, as tested by the growth of seedlings, small doses further, larger ones paralyse, the vital processes. W. D. H.

Physiological Action of Curare. By W. Nikolski and J. Dogiel (*Pflüger's Archiv*, **47**, 68—115).—The curare which reaches Europe is of different strengths; in many samples, calcium carbonate and phosphoric acid are present, and the preparations called "curarin" or "curarin sulphate" are by no means pure. The poison is not absorbed through the skin at all, and only with difficulty through mucous membranes; injected, however, under the skin or into the blood stream its effects are at once noticeable, and fairly equally so in all the classes of the animal kingdom with which experiments were performed, namely, mammals, birds, amphibians, reptiles, crabs, insects, and amœbæ. Curare has an influence on the central nervous system, the endings of motor nerves in voluntary muscles, in the cardiac and plain muscles, and also produces changes in the muscular tissues.

The point of injection makes considerable difference as to which part of the body is first affected. If the injection be made into the carotid artery, the cerebrum is affected first; if into a limb artery, paralysis of that limb is the first phenomenon produced.

The motor nerve endings are not all paralysed equally; thus plain muscles resist its action longest, and among voluntary muscles there are also differences found. Among different animals varying results are obtained, for instance, the drug acts less powerfully on the vasomotor centre of rabbits and cats than of dogs; applied to the conjunctiva of mammals, the pupil is not dilated, whereas in birds it is; atropine, on the other hand, produces pupillary enlargement in mammals, and not in birds. But if curare is injected into the circulation, the pupil of mammals is slightly widened. This action is thus probably not due to paralysis of the motor nerve endings in the *sphincter pupillæ*, but to some effect in the central nervous system.

The weakening or abolition of vagus influence on the heart is caused by smaller doses of curare in cats than in dogs and rabbits; the paralysis of the vagus endings in stomach and intestine occurs later, but unequally so in the three mammals mentioned.

The ultimate cause of the physiological action of curare is, doubtless, an alteration in the protoplasm of muscle and nerve, but this is not simultaneous nor equally great in the two tissues.

By washing out the curare from the voluntary muscles, paralysis passes off. There is a corresponding return of movements after irrigation in amœbæ and lymph corpuscles the activity of which has been stopped by curare.

Death in curare-poisoning in mammals is due to the effect of the drug on the respiratory centre, rather than on the motor nerve endings in the respiratory muscles. Curare subjected to the action of ozone loses its usual effects on the animal organism. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Action of Mineral Acids on the Lactic and Butyric Fermentations. By J. Effront (*Bull. Soc. Chim.* [3], **4**, 337—339).—The action of hydrochloric, hydrofluoric, and sulphuric acids on these fermentations in distillery worts is to enfeeble or to arrest their progress even when the wort is maintained at the most favourable temperature. Both the lactic and butyric fermentations are arrested by the addition of 0·025 gram of hydrogen fluoride per 100 c.c. of wort, and a similar effect is produced by the employment of 0·200 gram of hydrogen chloride or 0·300 gram of hydrogen sulphate. Data are given which confirm these results, and which show that the presence of hydrogen fluoride in worts to the extent of 0·020 gram per litre will prevent their acidifying, its action being especially unfavourable to the butyric fermentation. T. G. N.

Influence of Artificial Gastric Juice on the Acetic and Lactic Fermentations. By E. Hirschfeld (*Pflüger's Archiv*, **47**, 510—542).—If pure cultures of the *Bacillus aceticus* be grown in nutritive media made feebly acid with acetic acid, and containing 5 per cent. of alcohol, acetic acid is formed from the alcohol, the amount formed varying with the original quantity of the acid added. A small addition of hydrochloric acid (0·01 to 0·02 per cent.) causes an energetic increase of oxidation. Slightly larger quantities (0·03 to 0·5 per cent.) increase the oxidation, but not so vigorously, and a percentage of 0·6 to 0·7 stops it altogether. Pepsin *plus* hydrochloric acid acts in the same way as the acid alone. The feebler antibacterial action of the mixture observed in connection with the lactic acid fermentation is not observable with the acetic fermentation. The presence of phosphates and their nature has apparently no influence; but free phosphoric acid (0·1 per cent.) stops the oxidation of the alcohol. The percentage of hydrochloric acid necessary to stop the fermentation does not kill the bacteria, as they resume activity after neutralisation of the excess of acid. The bacteria are, however, killed by a percentage of 0·12 of the pepsin hydrochloric acid mixture.

The following conclusions were drawn from similar experiments on the lactic acid fermentation:—The *Bacillus acidi lactici* was grown in milk, and lactic acid forms most abundantly from the thirteenth to the twenty-fourth hour afterwards; as the acid increases, the bacteria become less active, as is shown by the following averages:—

First day, percentage of lactic acid	0·16
Second day, percentage of lactic acid	0·23
Third day, percentage of lactic acid	0·29

Small amounts of hydrochloric acid (0·01 to 0·02 per cent.) hinder the action markedly; larger quantities act in the same way until a percentage of 0·07 to 0·08 stops the fermentation altogether. Pepsin alone has no influence; but pepsin *plus* hydrochloric acid acts more energetically than the acid by itself, complete stoppage of the bacterial action being produced by 0·1 per cent. of the mixture. The same results were obtained with pure cultures of the bacillus. Phosphoric acid (0·2 per cent.) also stops the activity of the microorganism, but phosphates have no influence one way or the other.

These results, supported by most careful experiments, of which full details are given, place on a scientific basis the belief in the germicidal action of gastric juice so long held. W. D. H.

Behaviour of the Fatty Substances and the Rôle of the Lecithins during Normal Germination. By W. Maxwell (*Amer. Chem. J.*, **13**, 16—24; compare this vol., p. 511).—Experiments on the germination of *Phaseolus vulgaris*, *Gossyppium*, and *Zea mays* show that the young plants, during the early stage of their growth under the influence of light, are capable of utilising the inorganic phosphorus present in the seed for the formation of lecithins. At a later stage, when the plants are becoming independent of the seed, those substances are decomposed and utilised in the continued development of the organisms. G. T. M.

Change in the Nitrogenous Substances of Barley during Germination. By A. Hilger and F. van der Becke (*Bied. Centr.*, **19**, 860).—The substances examined were:—Barley, softened barley, fresh malt, and dried malt. The total nitrogen, the nitrogen of the constituents insoluble in water and that of the several soluble constituents, was determined; the percentage results are given in the following table:—

	Barley.	Softened barley.	Fresh malt.	Dried malt.
Water	14·470	43·341	47·958	8·431
Total nitrogen	1·801	1·750	1·751	1·542
Nitrogen of insoluble constituents	1·6789	1·6853	1·372	1·165
Nitrogen as albumin (soluble)	0·0600	0·0354	0·1571	0·1194
,, peptone	0·0046	0·0009	0·0058	0·0233
,, ammonium salts	0·0169	—	0·0290	0·0057
,, amido-acids	0·0417	0·0294	0·1417	0·2257
,, amides	—	—	0·0505	0·0029

In fresh malt and softened barley the total nitrogen is the same; in fresh malt 21·96 per cent. (of the total nitrogen) is soluble, but in softened barley only 3·75 per cent. During germination the soluble albumin, peptone, and amido-acids increase considerably. Dry malt contains less total nitrogen, owing to the falling away of the radicles. Soluble albumin, ammonium salts, and amides decrease; peptones and amido-acids increase. N. H. J. M.

Localisation of Active Principles in the Seeds of Cruciferæ. By L. GUIGNARD (*Compt. rend.* **111**, 920—923).—An account of an investigation, chiefly microscopical, made with a view to localise the various active principles in different cellules and tissues.

C. H. B.

Nitrogenous Bases in Seeds. By E. SCHULZE (*Zeit. physiol. Chem.*, **15**, 140—160).—The seeds of the vetch, *Vicia sativa*, were found to contain not only vicine, a base described by Ritthausen (Abstr., 1881, 1158), but also choline and betaïne. 20 kilos. of the seeds yielded 8—9 grams of choline platinochloride = 3—3·5 grams of choline, and 11—12 grams of betaïne; the latter was weighed partly as aurochloride, partly as the free base. In the course of the research, the observation was made that the choline platinochloride, when allowed to crystallise slowly from water, appears in the form of plates, but when crystallised rapidly, assumes the form of very slender prisms or needles; from alcohol it crystallises as regular octahedra.

From the seeds of the pea, *Pisum sativum*, the platinochloride of choline was also obtained (1 gram of choline from 3·5 kilos. of the seeds). Another base resembling betaïne was found in smaller quantity; it is, however, not betaïne, as its aurochloride contained only 41 per cent. of gold, instead of 43·1.

The question arises, do these compounds occur free, or combined in the seeds? It is possible that choline might occur in combination as lecithin, but certain considerations excluding this possibility, the conclusion is drawn that the bases are free in the seeds; they are, however, present in such small quantities that they do not have any poisonous action. W. D. H.

Composition of the Leaves of Maclura aurantiaca. By A. PIZZI (*Chem. Centr.*, 1890, ii, 766; from *Staz. sper. agr. ital.*, **18** 589—596).—The leaves of *Maclura aurantiaca* are used in the silk-worm culture as a substitute for the mulberry. The following is the analysis :—

Water	65·710
Fat	0·643
Proteïds	4·775
Non-proteïd nitrogenous substance	3·230
Cellulose	9·522
Sugar, starch, &c.	12·679
Mineral matter	3·421

The composition of the ash is :—

K_2O.	Na_2O.	MgO.	CaO.	Fe_2O_3.	SiO_2.	P_2O_5.	SO_3.	Cl.	Loss, &c.
9·244	6·156	6·727	25·732	3·814	26·247	17·543	2·405	1·327	1·805

The total nitrogen = 1·2841 per cent. Of the total proteïd substance, which amounts to 13·88 per cent. of the dry matter, 7·03 per cent. is undigested, and 6·85 digested by gastric juice. The composition of mulberry leaves, as given by several authors, and that of the leaves of *Maclura aurantiaca* is thus very similar. J. W. L.

The Behaviour of some Vegetable Substances towards Copper and some of its Compounds. By E. FORMENTO (*Bied. Centr.*, **19**, 844—845; from *Staz. sper. agr. ital.*, **18**, 686—693).—In vine culture, copper compounds are used as a cure for peronospora, it being assumed that the copper salt penetrates to the inside of the plants. The author made experiments to determine the manner and extent of the absorption of copper by vegetable tissues. When a solution of copper sulphate is mixed with clear, saturated lime-water, cupric hydroxide is not precipitated, but a more or less basic copper sulphate, according to the amount of copper sulphate present. The basic sulphates are soluble in water saturated with carbonic anhydride. The results of the author's experiments make it probable that copper can only reach the inner parts of plants by dialysis when a copper-lime mixture is used. When established inside the plant, copper compounds long resist the dissolving action of acids or of ammonia. An experiment in which an insoluble copper salt was separated by parchment paper from an acid sap showed that little or no copper passed through when free lime was present. N. H. J. M.

Acquisition of Atmospheric Nitrogen by Plants. By W. O. ATWATER and C. D. WOODS (*Amer. Chem. J.*, **13**, 42—63; compare this vol., p. 353).—The results of further experiments with peas, alfalfa, and with cereals, are described, and point to the following conclusions :—

1. That atmospheric nitrogen is undoubtedly acquired during the growth of peas and alfalfa, and that the amount of nitrogen gained increases with the number of root tubercles.

2. That the addition of soil-infusion is not necessary for the production of root tubercles, a fact which may be accounted for by supposing that the micro-organisms or their spores exist in the air, and are deposited in the pots where the plants grow.

3. That the cereals do not, as a rule, manifest the power of acquiring nitrogen from the air, nor are root tubercles formed on them, as in the case of leguminous plants. G. T. M.

The Nitrogenous Substance of Arable Soil. By L. L'Hôte (*Bied. Centr.*, **19**, 795—796; from *Jour. d'agric. pract.*, 1890, 365—366).—The following table shows the percentage of nitrogen in three soils, and in the organic matter of the soils separated by washing with water, and in the humic acid. This was extracted from the soil (previously extracted with weak hydrochloric acid to remove lime) with dilute aqueous potash (1 : 20), precipitated by hydrochloric acid, and dried in a vacuum over sulphuric acid.

•	Soil, natural state.	Soil treated with water.	Organic matter from 100 pts. of soil.	Humic acid (dried at 100°).
1. Garden soil	0·372	0·369	0·316	4·78
2. Arable soil (St. Pierre)	0·087	0·086	0·070	6·07
3. ,, (Serquigny)	0·140	0·136	0·089	5·41

The percentage of nitrogen in the humic acid approaches that obtained by Thénard with humic acid from rotten farmyard manure (*Compt. rend.*, 1857, 980). Humic acid in alkaline solution is absorbed by clay. The organic matter of soils is precipitated from its solutions by ferric chloride (compare Pigot, *Ann. Chim. Phys.*, 1864).

N. H. J. M.

Effect of Artificial Manuring on Clover Land and Meadows. By W. v. Knieriem (*Bied. Centr.*, **19**, 814—817; from *Balt. Wochenschr. f. Landw.*, 1890).—The experiments first described were made to ascertain the effect of different amounts of gypsum on clover land, and also the effect of early and late application of the manure. The application of 443 kilos. of gypsum per hectare on March 2 raised the yield by 45 per cent.; the same amount applied April 14 and May 15 raised the yield by 25 and by 4 per cent. respectively. With 665 kilos. per hectare (applied in March), the increase in produce over the unmanured plot was 42 per cent. In the next season the effect of gypsum had ceased. But it was observed that where no gypsum had been applied the first season, the grass was stronger the second season. This was due to the fact that the growth of clover had been so much increased by the gypsum that the grasses were kept back in their growth.

In other experiments, the plots were manured with (1) potash; (2) superphosphate; (3) bone meal; (4) potash and superphosphate; (5) superphosphate and ammonium sulphate; (6) lime. All those plots gave much more produce the first year than the unmanured plot did. The increase (taking both seasons) was 63 per cent. in No. 4; 52 per cent. in No. 5; 38 per cent. in No. 1; 30 per cent. in Nos. 2 and 3; and 27 per cent. in No. 6. In every case, except where superphosphate was used alone, the beneficial action of the manures extended to the second year's crop. N. H. J. M.

Experimental Plots of Mangold and Sugar Beet at Grignon, in 1890. By P. P. DEHÉRAIN (*Ann. Agronom.*, **16**, 542—558).—Five varieties of mangold, tankard, giant Vauriac, globe, Barres ovoid, and mammoth were grown; and Vilmorin's improved sugar beet from seed obtained direct from Vilmorin, and from the seed of the same variety saved at Grignon. For the sugar beet, 40,000 kilos. of farmyard manure per hectare was used; for the mangolds, 20,000 kilos. of farmyard manure per acre was applied to those plots which had been manured the previous year, and 30,000 to the rest; with 200 kilos. of Chili saltpetre in each case. The rows were 0·35 metre apart, and the roots 0·25 metre apart in the rows; by thus leaving the plants rather thick upon the ground, small or medium roots were obtained, which are much richer in solid matter and in sugar, and more free from nitrates than large roots. The average weights of the roots thus grown were: tankard, 900 grams; *géante de Vauriac*, 1070; globe, 860; *ovoïde des Barres*, 980; mammoth, 920; Vilmorin's sugar beet, 620; ditto, Grignon seed, 690. The roots were not only weighed, but sampled and analysed, in order to compare their true nutritive value, as shown in the total weight of dry matter *per hectare*, total sugar, and total nitrogenous organic matter; the nitrogen, as potassium nitrate, was also estimated in each case, the author considering the presence of much of this diuretic in the roots to be injurious to the cattle fed on them.

The sampling was done by taking 100 roots at random from each lot, and arranging them in three groups, large, medium, and small roots; if there were 20 large, 50 medium, and 30 small, 2, 5, and 3 average roots from their respective groups would be selected, and a cylindrical portion of each removed with a sound (as in cheese-tasting). The 500 grams or so thus obtained was cut into small pieces, weighed, dried, and the nitrogen estimations carried out on the dry matter. Organic nitrogen was estimated by Kjeldahl's method after removing nitric nitrogen by ebullition with ferrous chloride and hydrochloric acid; nitric nitrogen by Schloesing's method, in the hot water extract of the dry matter, after successive precipitation with lead acetate and sodium sulphate. The sugar was estimated in the juice by the shadow polarimeter in the usual way, and the density of the juice being taken, the sugar in the entire root was calculated.

The following table gives a *résumé* of the most important results of the trials:—

Arranging the varieties in order, under the heads (1) yield of dry matter; (2) yield of sugar; (3) yield of nitrogenous organic matter; and (4) poverty in potassium nitrate; and then adding up the positions under each head, the small-leaved globe is at the head, then tankard, giant Vauriac, Barres yellow, and mammoth, in the order named. Valuing the mangold roots at 15 fr. per tonne, the gross return is about 1200 fr. per hectare in each case; the manure is valued at 250 fr. and 350 fr. A plot unmanured since 1875 yielded 17,300 kilos. tankard mangolds per hectare only, and one receiving only 200 kilos. of potassium chloride yielded only 19,700 kilos. of the same roots. Valuing the sugar beet at 28 fr. to 37·5 fr. per tonne, according to density of juice, the gross return from Vilmorin's seed is 1552 fr.,

Plots.	Varieties.	Composition of root.		Yield per hectare.					
		Dry matter.	Sugar.	Roots.	Dry matter.	Sugar.	Nitrogen.		Potassium nitrate.
							Organic.	Nitric.	
		per cent.	per cent.	kilos.	kilos.	kilos.	kilos.	kilos.	kilos.
20, 22, 23	Barres' yellow ovoïd mangold	13·2	10·3	81,170	10,713	8359	124·0	25·7	190·8
24, 26	Tankard	14·2	9·9	81,800	11,704	8102	94·7	6·9	51·1
25, 27, 28	Vauriac giant yellow.............	14·4	9·0	82,930	11,942	7430	128·9	20·2	147·2
29, 30, 32	Small-leaved globe	14·8	9·9	81,000	11,987	8018	119·8	10·7	79·5
31	Mammoth......................	14·2	10·0	77,400	10,990	7740	102·2	7.6	62·2
71, 72, 73	Vilmorin's improved sugar beet ...	22·9	16·2	43,470	9,959	7044	88·5	5·9	42·4
74, 75	Ditto, from Grignon seed	23·2	15·1	46,650	10,822	7043	87·6	7·5	54·3

and from Grignon seed, 1351 fr. per hectare; the manure is valued at 400 fr. It is remarkable that rather more sugar per hectare is obtained from the mangold crop than from the sugar beet, but as against this advantage, the gross weight of the crop is nearly double, and the foreign matter and potassium nitrate associated with the sugar much larger. Distillers find it to their advantage to grow a sugar beet (*betterave à collet rose*) poorer in sugar than Vilmorin's improved, but yielding a larger crop, more sugar per hectare, and more pulp for cattle.

A cow eating 25 kilos. yellow ovoid mangolds per day would consume 50 grams of nitre, a quantity the author considers injurious. He quotes Barral's analyses of the enormous roots sent over for show from England, of Sutton's mammoth, Berkshire, and oxheart varieties, which compare very disadvantageously with the small roots obtained by growing the same or similar varieties closer together. Thus Sutton's mammoth roots, averaging 14,150 grams each, contained only 5·81 per cent. dry matter, and the dry matter contained as much as 13·89 per cent. of potassium nitrate, and as little as 17·21 per cent. of sugar, with 22·13 per cent. of proteïds. J. M. H. M.

Analytical Chemistry.

Detection of Chlorides, Bromides, and Iodides. By G. Denigès (*Bull. Soc. Chim.* [3], **4**, 481—483).—The mixture is strongly acidified with sulphuric acid and the iodine and bromine are separately liberated by successive treatment with ferric chloride and potassium chromate. The iodine is characterised by starch paper, and the bromine by introducing a rod moistened with sodium hydroxide solution into the tube in which the halogen is being evolved. On then placing the rod in aniline water, the hypobromite formed gives an orange-yellow coloration. If all three halogens are present, the iodine and bromine must be removed by continuous boiling of the acidified solution with potassium chromate; potassium permanganate is then added, and the chlorine evolved tested with a rod dipped in soda solution, as in the case of bromine; it gives a violet coloration with aniline water. T. G. N.

Volumetric Estimation of Chlorides in Urine. By A. Corvi (*Chem. Centr.*, 1890, ii, 795; *L'Orosi*, **13**, 253—255).—The chloride is precipitated with an excess of N/10 solution of silver nitrate, and the excess of silver determined by titration with potassium ferrocyanide solution of equivalent strength; ferric sulphate is employed as indicator.

10 c.c. of urine is acidified with a few drops of nitric acid, and 50 c.c. of the silver chloride solution is added. The volume of the solution is noted, then filtered, and one third of the filtrate titrated with ferrocyanide. J. W. L.

Estimation of Nitric and Nitrous Acids in Potable Waters. By M. ROSENFELD (*Zeit. anal. Chem.*, **29**, 661—664).—Under certain conditions, the reaction of nitric and nitrous acids with pyrogallol affords one of the most sensitive means for their detection and approximate estimation. 3 c.c. of the water to be tested is rapidly mixed in a conical test glass with 6 c.c. of concentrated sulphuric acid; one drop of a 1 per cent. solution of pyrogallol is then added, and cautiously mixed with the upper two-thirds of the liquid. In a few minutes or immediately, according to the amount of nitric acid present, a dark-brown to violet colour is produced. As little as 1 milligram of nitric anhydride per litre can be detected, and up to 15 milligrams per litre comparisons of the depth of colour with standards furnish a roughly approximate estimation. The test-glass for the operation must not be wiped, nor must more than one drop of the pyrogallol solution be used, unless the colour disappears on shaking, which may happen when much nitrate is present.

For nitrous acid, a solution is made containing 0·5 gram of pyrogallol, 90 c.c. of water, and 10 c.c. of sulphuric acid. Of this mixture, 2 c.c. is added to 100 c.c. of the water in a cylinder. 0·04 milligram of nitrous anhydride in the 100 c.c. produces a yellow colour immediately; with 0·01 milligram, the colour develops only in seven hours. Up to 0·05 milligram, a difference of 0·005 milligram is perceptible. M. J. S.

Detection of Carbonic Oxide in Blood. By M. RUBNER (*Zeit. anal. Chem.*, **30**, 112; from *Arch. Hygiene*, **10**, 397).—The blood is shaken for a minute in a test-tube with four or five volumes of lead acetate solution. Blood containing carbonic oxide remains red, whilst normal blood becomes brownish, and ultimately chocolate-brown and greyish-brown. The difference is still recognisable when the carbonic oxide blood is diluted with eight or nine volumes of normal blood. M. J. S.

Analytical Methods for Alkali Works. By G. LUNGE (*J. Soc. Chem. Ind.*, **9**, 1013—1019).—*Estimation of Sulphur in Pyrites.*—The author's method (Abstr., 1881, 193) adopted in the "Pocket Book for Alkali Makers," although severely criticised by Jannasch and Richards (Abstr., 1889, 926), has stood the test of practical application since its introduction in 1881. Jannasch confused the method with an older process, and subsequently acknowledged that the author's 1881 method gave results agreeing closely with the numbers obtained by his own method (Abstr., 1889, 1244). For estimating the sulphur in burnt pyrites, the author now prefers the method recommended by Watson (Abstr., 1889, 306).

Testing Pyrites Burner Gases.—Reich's method can no longer be considered accurate, as it has been proved by many observers that burner gases contain sulphuric anhydride. The author therefore proposes to estimate the total sulphur acids in burner gases by absorption in a solution of soda, using phenolphthaleïn as indicator. For this purpose, Reich's apparatus is employed, but it is found desirable to modify the absorbing bottle by sealing the inlet-tube for the gas at the bottom, and perforating it below the level of the liquid with several pin-holes, through which the gases issue in minute bubbles instead of one large bubble. In calculating the results, it is necessary to take careful readings of the thermometer and barometer for correcting the volume of gas aspirated.

Testing the Chamber Exit Gases.—The well-known prescriptions of the English Alkali Makers' Association can be greatly simplified by introducing the above process with caustic soda and phenolphthaleïn, which has already been done with great practical success. It has also been found necessary to revise the methods for estimating the nitric oxide in the exit gases. With regard to the best form of absorbing apparatus, the author after many trials decided in favour of the 10-bulb tube, which for greater security may be enlarged to 15 bulbs. Concerning the best absorbent, the final conclusion was that so far no better mode of estimating the nitric oxide contained in the exit gases is known than that of passing them through a titrated solution of potassium permanganate strongly acidified with sulphuric acid, and contained in a 15-bulb tube. At the end of the operation an excess of a titrated solution of ferrous sulphate is added, and the mixture again titrated with standard permanganate.

Estimation of Free Lime in Black Ash.—50 grams of the sample is quickly, but thoroughly, ground to a fine powder, which is transferred to a litre flask, and covered with lukewarm distilled water freed from carbonic anhydride by boiling. The mixture is at once well shaken, and the agitation is repeated several times during two hours. This prevents the formation of a hard cake at the bottom which does not further disintegrate. The flask is then filled up to the mark, and special samples are taken out with a pipette for the estimation of free lime, and if required for total lime (see below), the contents being thoroughly shaken up each time. In the test for free lime, the contents of the pipette are run into a beaker, an excess of barium chloride is then added, and the solution titrated in the cold with N/5 oxalic acid, using phenolphthaleïn as indicator.

Estimation of Total Soda and Total Lime in Black Ash.—In the test for total lime, the contents of the pipette are transferred to an Erlenmeyer flask, mixed with a few c.c. of strong hydrochloric acid and boiled. A drop of methyl-orange is now added, and sodium carbonate solution run in until the pink colour has just disappeared. 30 c.c. of N/5 sodium carbonate is then added from a burette, and the mixture boiled to precipitate all the calcium carbonate. This is then washed into a 200-c.c. flask, and 100 c.c. of the clear portion titrated with N/5 hydrochloric acid to determine the quantity of sodium carbonate taken up by the lime present. For the ordinary black ash tests, the clear portion of the original black ash solution is used.

Estimation of available Soda in Alkali Waste.—At some Lancashire works, the aqueous extract is treated with carbonic anhydride, the mixture boiled to decompose the calcium hydrogen carbonate, and the clear solution titrated. The author finds that this method gives concordant results practically identical with those obtained even more quickly by zinc carbonate, which requires only 15 minutes' boiling, whilst the treatment with carbonic anhydride must be carried on for at least one hour (less being insufficient).

Estimation of Hydrogen Sulphide and Sulphurous Anhydride in the same Gaseous Mixture.—The author proposes to pass the gases through a bulb apparatus containing iodine solution, followed by another apparatus containing a little standard soda solution. At the end of the operation the contents of both apparatus are united. The mixture should have an acid reaction, otherwise it must be acidified with a known quantity of standard acid. The unused iodine is then estimated by means of sodium thiosulphate, after which methyl-orange is added, and standard soda run in to neutral reaction. This method gives all data required for estimating sulphurous anhydride and hydrogen sulphide, since the latter liberates only its equivalent of hydrogen iodide, whilst the former, in addition to its equivalent of hydrogen iodide, also yields an equivalent quantity of sulphuric acid. If m represents the difference between the quantity of iodine solution originally employed and that of thiosulphate used in retitrating, n the decinormal soda solution originally employed, and o the quantity of soda used in the end for establishing neutrality, the quantity of sulphur present is found by the following expressions :—

$$\begin{aligned}\text{S in } H_2S \text{ and } SO_2 &= 0{\cdot}0016m.\\ \text{S in } SO_2 &= 0{\cdot}0016(n + o - m).\end{aligned}$$

D. B.

Estimation of Available Soda in Commercial Caustic Soda. By J. WATSON (*J. Soc. Chem. Ind.*, **9**, 1107—1108).—In the preceding abstract, Lunge, in referring to the method used at some Lancashire works, mentions that less than one hour's treatment with carbonic anhydride is not sufficient to effect the necessary reaction. The author has used the method in question for a number of years, and has always obtained satisfactory results by proceeding in the following manner :—20 grams of waste is treated with about 150 to 200 c.c. of warm distilled water; after stirring and allowing to remain for about an hour, the clear liquid is decanted, and carbonic anhydride passed in for three to five minutes. This at first causes a milkiness, owing to precipitation of calcium carbonate, the solution subsequently becomes clear as the carbonate is dissolved as calcium hydrogen carbonate in the excess of carbonic anhydride, hydrogen sulphide is then evolved, and at this point the author considers that sufficient gas has been passed through the solution. He then evaporates to at least half the original volume, filters off, and washes the calcium carbonate, titrating the alkali in the filtrate with a dilute standard acid, and using methyl-orange as indicator.

D. B.

Test for Thiosulphate in Sodium Hydrogen Carbonate. By F. MUSSET (*Zeit. anal. Chem.*, **30**, 45).—5 grams of the salt is rubbed with 0·1 gram of calomel and two drops of water. The smallest trace of thiosulphate reveals itself by blackening the calomel.

M. J. S.

Analysis of Commercial Sodium Fluoride. By E. HINTZ and H. WEBER (*Zeit. anal. Chem.*, **30**, 30—33).—A specimen of this material was strongly alkaline, and showed by qualitative analysis the presence of much sodium carbonate and silica, with smaller quantities of sulphates and chlorides, potassium, calcium, magnesium, aluminium, and ferric oxides.

Estimation of Silica and Fluorine.—About 2—3 grams of the sample was boiled with ammonium carbonate in a platinum basin, and the insoluble residue preserved. The filtrate was treated with a solution of zinc oxide in ammonia, and the ammonia boiled off; the precipitate was then dissolved in nitric acid, and the silica rendered insoluble by evaporation. The united portions of impure silica were fused with sodium carbonate and recovered by evaporation with acid. The filtrate from the zinc precipitate was precipitated hot with calcium chloride, and the precipitate thus produced, consisting of calcium carbonate and fluoride, was, after washing and ignition, decomposed by acetic acid; the excess of acetic acid was evaporated, and the calcium fluoride washed, ignited, and weighed.

For estimating the sulphuric acid, 20 grams was heated with water and made up to a litre; a portion of the clear solution was acidified in a platinum basin, precipitated with barium chloride, filtered in a platinum funnel, and the precipitate fused with sodium carbonate for its purification. Similarly, for the estimation of the chlorine by precipitation with silver nitrate, the operations were performed in platinum. The carbonic anhydride was expelled by boiling with tartaric acid, collected, and weighed.

For the various bases, the substance was evaporated with sulphuric acid and the metals separated by ordinary processes. The water was estimated by heating a weighed quantity in a stream of dry air and collecting the water in a calcium chloride tube.

For estimating that portion of the silica present as sand, the insoluble residue of the original substance was boiled with sodium carbonate and hydroxide, and the insoluble matter purified by hydrochloric acid.

The composition found was as follows:—

Sodium fluoride	65·65
„ chloride	0·74
„ carbonate	13·89
„ sulphate	1·96
Potassium sulphate	0·74
Soda (combined with silica)	1·50
Silica (partly combined with soda)	10·11
Calcium carbonate	0·25
Magnesium carbonate	0·32
Ferric oxide	0·48
Alumina	0·17
Water	3·97
	99·78

M. J. S.

Analysis of Commercial Barium Hydroxide. By E. HINTZ and H. WEBER (*Zeit. anal. Chem.*, **30**, 24—29).—A specimen examined by the authors contained barium hydroxide, carbonate, sulphate, thiosulphate, sulphide, and sulphite. On treatment with water, the carbonate, sulphate, all the sulphite, and part of the thiosulphate remained undissolved.

About 20 grams of the substance was treated with boiling water, made up to 500 c.c., allowed to deposit, and the total barium in 50 c.c. of the clear solution determined gravimetrically. For the sulphide estimation, 250 c.c. was poured into pure potash, to which a few drops of lead acetate had been added. The precipitate of lead sulphide and barium carbonate was oxidised by bromine and hydrochloric acid, and the lead sulphide thus converted into barium sulphate. In this operation it is necessary to use enough potash to prevent precipitation of lead thiosulphate; also, if much sulphide is present, the barium sulphate precipitate may contain lead sulphate, in which case it must be fused with alkaline carbonates, and the aqueous solution treated with carbonic anhydride before reprecipitating as barium sulphate. The filtrate from the lead sulphide was now oxidised by bromine and hydrochloric acid, to convert the thiosulphate into barium sulphate. This precipitate may also contain lead. The difference between the total soluble barium and that found as sulphide and thiosulphate gave the amount of hydroxide.

For estimating the sulphate, 5 grams was boiled with dilute hydrochloric acid in a stream of carbonic anhydride. The whole was evaporated to dryness, taken up with water and a few drops of hydrochloric acid, and the undissolved portion fused with alkaline carbonates; the sulphuric acid was then precipitated from the solution of the fusion. For the sulphite and undissolved thiosulphate, the insoluble residue of 10 grams was treated with hydrochloric acid, in a flask connected with an inverted condenser and two Péligot tubes containing bromine and hydrochloric acid, whilst carbonic anhydride was passed through the apparatus. The sulphurous anhydride from both the sulphite and thiosulphate was retained by the bromine, and, after evaporating to dryness, was weighed as barium sulphate. The thiosulphate was estimated from the sulphur left in the decomposition flask with barium sulphate. It was oxidised by bromine and hydrochloric acid, and weighed after fusion with carbonates and reprecipitation.

The carbonate was estimated by mixing 10 grams of the substance with a strong solution of potassium permanganate and decomposing by nitric acid. The carbonic anhydride evolved was passed through a tube containing pumice stone moistened with permanganate and inserted between the evolution flask and the absorption tube.

The composition of the specimen analysed was as follows:—

Barium hydroxide, $Ba(OH_2) + 8H_2O$	94·31	per cent.
,, sulphate	0·52	,,
,, sulphite	0·07	,,
,, thiosulphate	0·70	,,
,, carbonate	1·75	,,
,, sulphide	0·04	,,

M. J. S.

Separation of Barium from Calcium. By R. FRESENIUS (*Zeit. anal. Chem.*, **30**, 18—23).—Precipitation by normal ammonium chromate from a dilute, hot solution of the two chlorides, feebly acidified with acetic acid, filtration after cooling, and washing, first with ammonium chromate and then with warm water, gave a fairly satisfactory result, the baryta found being 0·3127 gram, instead of 0·3104. A little calcium was therefore retained by the precipitate, and this was also the case when more acetic acid was used (2 c.c. to 200 c.c. of solution containing 0·5 gram of the bases), together with 6 grams of ammonium acetate, and the precipitate was most thoroughly washed by digesting with hot water and filtering after cooling. By double precipitation, a slight deficiency of barium and a trifling excess of calcium were obtained; the separation was, however, more nearly perfect. The first precipitate was dissolved in a little nitric acid, and the diluted solution precipitated by ammonium acetate and chromate.

Precipitation with hydrofluosilicic acid and washing with dilute alcohol did not give complete separation, a little calcium being precipitated. A more satisfactory, but still not quite perfect, separation resulted when the precipitate, after slight washing with weak alcohol, was repeatedly digested with cold water, the aqueous washings concentrated, reprecipitated with 4 drops of hydrofluosilicic acid and one-third volume of alcohol, and the small precipitate added to the main one. A combined method, precisely similar to that finally adopted for strontium (Abstr., 1890, 925), gives an almost perfect separation.

M. J. S.

Detection and Estimation of small quantities of Aluminium in Iron and Steel. By A. CARNOT (*Compt. rend.*, **111**, 914—916).—10 grams of the metal is dissolved in hydrochloric acid in a platinum vessel, diluted, and filtered. The greater part of the free acid is nearly neutralised, first with ammonia and afterwards with sodium carbonate. Sodium thiosulphate is added, and when the violet coloration has completely disappeared and the solution contains only ferrous salt, 2 to 3 c.c. of a saturated solution of sodium phosphate and about 20 c.c. of a solution of sodium acetate are added, and the liquid is boiled until all sulphurous anhydride is expelled. The precipitate, which consists chiefly of aluminium phosphate, with some silica and ferric phosphate, is washed with boiling water, redissolved in dilute hydrochloric acid, the silica filtered off, the filtrate diluted to 100 c.c., and the precipitation repeated in precisely the same manner. The precipitate is washed with boiling water, dried, and weighed.

C. H. B.

Estimation of Ferric Oxide and Alumina in Phosphates. By V. GRUBER (*Zeit. anal. Chem.*, **30**, 9—14).—The "conventional method" yields high results at the first precipitation, owing to the retention of much calcium phosphate with the insoluble phosphates, whilst after a second treatment, the results are too low, in consequence of the solubility of aluminium phosphate in acetic acid. The author has not been able to obtain accurate results by Stutzer's method, in which the phosphoric acid is removed by molybdate. Glaser's method, however (Abstr., 1890, 420), affords results which are in all cases concordant, and has been accepted by the Conference of the Representatives of the Artificial Manure Industry, held at Bremen. Only in cases where it is desirable to estimate the iron and aluminium separately, is there any necessity for the removal of the phosphoric acid by molybdate. M. J. S.

Dry Assay of Tin Ores. By H. O. Hoffmann (*Chem. News*, **62**, 276—277, 291—293, 300—302, 316—317; continued from p. 246).—Rickett's method for the assay of the ores containing silica only, namely, fusion with hæmatite, potassium cyanide, and charcoal in a luted, charcoal-lined crucible, is regarded as of little value to the assayer, beyond substantiating the fact that iron carries down all the tin. With such ores, it is best to separate the black tin by vanning, and then reduce it with potassium cyanide. Mitchell's method of fusion with ferric oxide, fluorspar, and charcoal for the assay of siliceous tin ores and slags, gave neither buttons nor prills in the hands of the author, who recommends, in preference, decomposing the finely pulverised slag with sodium or potassium hydrogen sulphate and treating with acid; the tin is easily estimated in the resulting mixture of stannic oxide and silica. Experiments with the method due to Bloxam, namely, mixing 5 grams of ore with 5 grams each of potassium cyanide and ferrocyanide, reserving 5 grams of the former salt for the top of the crucible, give results differing by 1 gram.

By the Cornish methods of assaying black tin by heating in charcoal-lined crucibles, with or without anthracite and fluorspar, unsatisfactory results were obtained, owing to the difficulty of separating the heavy slag from the fine tin. Of all the various methods and modifications recommended by different authorities, the author is of opinion that the German method and the method of fusion with potassium cyanide are the only two which give entirely satisfactory results.

The next point taken into consideration is the influence of associated minerals on the working of these two methods. Pulverised quartz, felspar (albite), mica (muscovite), garnet (almandite), tourmaline, and columbite were respectively mixed with black tin in different proportions, and submitted to assay; the results are tabulated and described.

When the German method was used, the quartz decreased the proportion of soft slag formed on the top of the borax slag, which became finer, harder, more plentiful, and less vitreous as the silica increased, whilst the buttons separated well, but the yield of tin was diminished; mixing the ore with basic flux proved very detrimental; felspar gave slags similar to those with quartz, but more stony and adhesive to the button; the latter was dark, brittle, hard to cut, and contained iron, whilst some tin had slagged. Mica and tourmaline produced a similar, but more marked, effect than felspar, more iron was reduced and more tin lost, and when the proportions of added mineral amounted to 50 per cent., no proper fusion ensued; with the garnet, the salt slags were less crystalline than usual, the borax slags became stony, tough, and opaque, the buttons all dark-grey, hard to cut, brittle, and rich in iron, the results, in the author's opinion, were uniform, and appear to indicate that if tin is to be recovered from siliceous ore as an alloy, a basic silicate of iron is the best flux for the purpose; with columbite, the salt slags were stony and dull, the borax slags brittle, vitreous, and of resinous lustre, whilst the buttons were dark-grey, becoming black and ferruginous, the quantity of iron increasing with the percentage of columbite added.

When the cyanide process was employed, quartz gave lustrous, coarsely crystalline slags, increasing in hardness as the quantity of quartz was increased, the appearance of the button being unaltered by the silica; felspar and mica produced but little effect beyond making the lower slag more porous, the buttons were unaltered, and the loss of tin was less than in the German process; tourmaline had no effect; garnet coloured the lower slag, which increased in quantity with the garnet added, the button was ferruginous, but some tin slagged; columbite gave an increasingly porous and coloured under slag, and a white, bright, malleable, soft button, containing but little iron.

With regard to the interference of impurities, the cyanide process therefore comes off the best, but the German method is cheaper.

Taking into account the interference of impurities, it is important to remove them as far as possible before the assay; most of them, the non-metallic ones, can be removed by crushing, sizing, and panning, the metallic ones by roasting, chilling, and treating with nitrohydrochloric acid. This also removes garnets, and metallic iron coming from the grinding implements; the concentrates may, if necessary, be treated with hydrofluoric acid; the roasting, moreover, makes some samples of cassiterite more friable and more readily reducible. Altogether, it is considered that by the careful use of the few correct methods of preparation and assaying, the dry assay of purified black tin and tin ores will give more accurate results than the dry assay of any other base metal. D. A. L.

Analysis of Brandy and Alcohol. By E. MOHLER (*Compt. rend.*, **112**, 53—55).—*Ethereal salts.*—100 c.c. of the distilled alcohol is boiled for an hour with 20 c.c. of decinormal potash in a reflux apparatus; the excess of potash is determined, and the rest is calculated to ethyl acetate.

Aldehydes are estimated by means of the coloration with rosaniline bisulphite, the intensity of the colour of the solution examined being compared, by means of a Duboscq colorimeter, with the coloration given by a solution of aldehyde of known strength; 10 c.c. of a 0·01 per cent. solution of acetaldehyde in alcohol of 50° is a convenient quantity to employ as a first standard.

Higher alcohols.—100 c.c. of the distilled liquid is mixed with 1 c.c. of aniline and 1 c.c. of phosphoric acid of 45°B to retain the aldehydes, and after cohobating for an hour, is distilled to dryness in a solution of salt. The distillate is treated with sulphuric acid of 66°, and the coloration is compared with that given by an alcohol containing 0·250 gram of isobutyl alcohol per litre.

Nitrogen compounds.—100 c.c. of the undistilled liquid is distilled to dryness with 2 c.c. of a solution of phosphoric acid of 45° B, the residue is dissolved in about 1000 c.c. of distilled water, mixed with 10 grams of sodium carbonate, and distilled, the distillate being Nesslerised. Alkaline potassium permanganate is then added, and distillation and Nesslerising is repeated. The first operation gives the nitrogen present as ammonium compounds and amides, and the second gives the nitrogen existing as pyridine bases and alkaloïds.

Several analyses of brandy and alcohol are given. C. H. B.

Estimation of Sugar in the Blood. By F. SCHENCK (*Pflüger's Archiv*, **47**, 621—629).—In connection with a previous communication on this subject (this vol., p. 350), the author defends himself against criticisms passed on his method by Salkowski (*Centr. med. Wiss.*, 1890, No. 17), and Röhmann (*Centr. Physiol.*, 1890, Heft 1), but admits, after carrying out experiments on dialysis, that probably the sugar and the proteïd are not in chemical combination.

W. D. H.

Testing Cassia Oil. By E. HIRSCHSOHN (*Zeit. anal. Chem.*, **30**, 99—103; from *Pharm. Zeit. Russland*, **29**, 225).—1. The oil is shaken in a graduated tube with three volumes of light petroleum (0·65). A diminution in its volume indicates the presence of other ethereal or fat oils, or of resin or kerosene; an increase would probably be due to the presence of much castor oil. 2. The petroleum extract is shaken with copper hydroxide. A blue solution indicates colophony or copaiba balsam. 3. One volume of the oil must give a clear or merely opaline solution with three volumes of 70 per cent. alcohol at 15°. A turbidity or sediment indicates the presence of petroleum, or of foreign ethereal or fatty oils, or of a large excess of colophony. 4. The alcoholic solution from 3 is poured into half its volume of a cold saturated solution of lead acetate in 70 per cent. alcohol. No precipitate should be produced.

To estimate the cinnamaldehyde in the oil, 75 grams of it is well shaken in a capacious flask with 300 c.c. of a boiling, 30 per cent. solution of sodium hydrogen sulphite. After a short repose, 200 c.c. of hot water is added, and the whole is warmed on the water-bath until the compound of the aldehyde with the sulphite is completely dissolved, when the constituents other than aldehyde and all the impurities form an oily layer on the surface. After cooling, this oily layer is dissolved in ether, and the filtered ethereal solution is evaporated in a tared beaker as rapidly as possible on the water-bath, and is weighed at intervals of ten minutes. When two weighings differ by no more than 0·3 gram, the last but one is taken as that of the non-aldehydic substances present. The cinnamaldehyde is known from the difference. Cinnamic acid, if present, may be removed by shaking the oil with hot sodium carbonate solution, and the amount found deducted from that of the aldehyde ascertained as above.

A rough technical method for the same purpose consists in placing 10 c.c. of the oil in a special flask of about 100 c.c. capacity, with a cylindrical neck graduated in tenths of a cubic centimetre. The oil is treated in the flask with the sodium hydrogen sulphite, and when the crystalline sulphite has been completely dissolved by prolonged heating on the water-bath, and the non-aldehyde constituents have formed a clear oily layer on the surface, they are driven up into the graduated neck by cautious addition of sulphite solution, and their volume read off when cold. The specific gravity of the non-aldehydic oil may, without serious error, be taken as 1·06 at 20°, or identical with that of the original cassia oil. A good cassia oil should contain at least 75 per cent. of cinnamaldehyde. M. J. S.

Estimation of Acidity in Lubricating Oils. By HOLDE (*Chem. Centr.*, 1890, ii, 568; from *Mitt. königˇ. techn. Vers.-Anstalt, Berlin*, 1890, 151—153).—In the case of light-coloured oils, the author recommends measuring exactly 10 c.c. into a 300 c.c. Erlenmeyer flask, washing the measure with a mixture of 8 parts of ether and 2 parts of absolute alcohol containing a little phenolphthaleïn, and titrating with standard alcoholic soda (1 c.c. of which = 0·005 gram SO_3).

In the case of dark-coloured oils, where the colour would prevent the alkaline phenolphthaleïn from being seen, the author recommends that 20 c.c. of the oil should be agitated with 50 c.c. of absolute alcohol, and after the oil has again separated from the alcoholic extract, 25 c.c. of the latter is titrated with the alcoholic sodium hydroxide, after addition of 20 c.c. of the alcohol-ether mixture. If the amount of acidity is more than 0·03 per cent. (calculated as sulphuric anhydride), it is recommended to decant the remainder of the alcohol from the oil and to again extract with a further quantity of 50 c.c. of absolute alcohol.

Instead of using a burette marked in cubic centimetres, the author recommends one graduated in such volumes as are equivalent to percentages of acidity (= SO_3). J. W. L.

Estimation of Mineral Oils in Fat Oils. By A. GRITTNER (*Zeit. ang. Chem.*, 1890, 261).—The following slight modification of Horn's method (*Zeit. ang. Chem.*, 1888, 458) allows the estimation to be made satisfactorily when the proportion of mineral oil is large. 2 or 3 grams of the sample is saponified in a small porcelain basin on the water-bath by 20 c.c. of alcoholic soda containing 20 to 25 grams of sodium hydroxide per litre of 95 per cent. alcohol. Heating and stirring are continued until the alcohol is entirely expelled, and then a quantity of sand (purified by hydrochloric acid) is mixed in. The mass is then treated in a Soxhlet's extractor with chloroform (purified by distillation with concentrated sulphuric acid), and the dissolved oil is dried at 100° after distilling off the chloroform. M. J. S.

Estimation of Oils, Fats, &c. By T. T. P. B. WARREN (*Chem. News*, **62**, 215, 251).—In the first communication, equations are given for calculating, from data supplied by iodine absorption and also Maumené's reaction, the proportions of constituent oils, of which the presence has been undoubtedly ascertained, in mixtures of two or three oils. In the second communication, various oils, &c., are classified, according to their behaviour with sulphur chloride:—The first division contains those which give an insoluble product; this is of an elastic, spongy nature (except in the case of olive and cottonseed oils, from which the sulphur at first dissolved separates on cooling) and is soluble in ether; but caoutchouc and gutta-percha are precipitated from such solutions by a few drops of alcohol; the following are the oils, &c., which have come under the author's notice, and behave in this manner:—Olive, poppy, "*papav. somnif.*," "*glaucium* *flav.*," almond, earthnut, walnut, sesame, nigerseed, castor, rapeseed, cotton, beechmast, and hempseed oils, also caoutchouc, gutta-percha, and allied substances, and the resins naturally associated with them. The second division includes those that do not behave in this manner, namely, sperm, whale, cod, lard, cocoanut, palm, and resin oils; spermaceti, lard, butter, beeswax, beef and mutton fat, pine resins, turpentine, Japan wax, petroleum and paraffin homologues; coal-tar, shale oil, and similar distillates from minerals, as well as glycerol and the fatty acids derived from the oils of the first division. Hence, oxidised, blown, or old oils of the first division produce more soluble products than the fresh oils. Oils of the second division yield less magma than oils of the first division; some of the former, petroleum and coal-tar distillates, for instance, simply act as solvents for the sulphur chloride. Any nitroglycerol, formed by the use of nitric acid, must be carefully removed when making tests. D. A. L.

Examination of Oils, Fats, and Allied Substances. By T. T. P. B. Warren (*Chem. News*, **62**, 288).—Points regarded as of importance in the examination of an oil are the specific gravity, the expansibility, and absorption of oxygen. The sp. gr. is taken in a bottle at 60° F. for thin oils; at 100° F. for thick oils, fats, &c. The expansion of an oil proceeds in a geometrical ratio giving a logarithmic curve in which the axes x and y follow a regular rate of variation; therefore, in case there is any irregularity in the expansion of an oil, the temperature at which it occurs should be noted. For the oxygen absorption, the oil is exposed to a known volume of the gas, which is subsequently remeasured and analysed; the carbonic anhydride represents the glycerol set free, any further deficiency of oxygen being due to retention of that gas by the oil and fatty acids. D. A. L.

Adulteration of Olive Oil. By R. Brullé (*Compt. rend.*, **111**, 977).—10 c.c. of the oil is heated in a water-bath for half an hour with 5 c.c. of a 25 per cent. solution of silver nitrate in ethyl alcohol of 90°. Pure olive oil remains transparent and aquires a grass-green colour; earth-nut oil acquires a reddish-brown tint; oil of sesame acquires a very deep rum colour; colza becomes black and then dirty green; linseed oil acquires a deep reddish tint; cotton-seed oil becomes black; poppy-seed oil becomes greenish-black; oil of camelina becomes black, but in daylight, if the tube is inclined, it is seen to have a brick-red tint. C. H. B.

Analysis of Olive Oil and Seed Oils, Butter, and Margarine. By R. Brullé (*Compt. rend.*, **112**, 105—106).—12 c.c. of the oil is mixed with 5 c.c. of a 2·5 per cent. solution of silver nitrate in alcohol of 95°, and the mixture is heated in a test tube in a water-bath for 10 to 20 minutes. The oil must be filtered if it is not perfectly transparent.

The purest olive oil acquires a beautiful, delicate green colour; inferior olive oil at first blackens slightly or becomes pale red, but the colour soon changes to an intense green. Cotton-seed oil becomes quite black; earth-nut oil is at first red-brown, but afterwards becomes green and turbid; oil of sesame becomes deep brown-red and does not turn green; colza oil and poppy-seed oil acquire a yellow-green colour and become turbid. The reaction will detect from 5 to 10 per cent. of impurity in olive oil.

Under these conditions, genuine butter from various sources retains its original colour, but butter containing margarine becomes brick-red. The reaction is distinct with 5 per cent. of margarine, and with 10 per cent. the red tint is strongly marked. C. H. B.

Composition of Butter Fat, as determined by the Reichert-Wollny Method.—By P. VIETH (*Milch. Zeit.*, **18**, 541—545).—Although the method of determining the amount of volatile fatty acids in butter fat originally devised by Reichert and Meisl and afterwards modified by Wollny gives results which are perfectly concordant with one another, the amount of volatile fatty acids obtained from the fat of different samples of butter has varied within such wide limits, that the value of the method for the determination of the admixture of foreign fats with butter is correspondingly decreased. The results obtained by the author confirm those of other chemists.

There remains, therefore, the fact that butter fat varies in composition, and it was principally with a view to detecting, if possible, the cause of the variations that the author's experiments were made. The analysis of a sample of butter fat, received from Kiel on behalf of the "Kommission zur Feststellung der besten Butter-Prüfungs Methode," shows how little the amount of volatile fatty acids changes by lapse of time. (The results in this, as in all other cases, are expressed in c.c. of N/10 alkali, equivalent to the volatile fatty acids obtained from 5 grams of butter fat):—(*a.*) September 20th, 1888 = 31·8, 31·6, 31·8, 31·9, 31·9. (*b.*) January 17th, 1889 = 32·1. (*c.*) May 2nd, 1889 = 32·1.

From November, 1888, to May, 1889, 59 samples of butter fat were analysed. Of 28 samples of French butter the lowest value for volatile acids found was 26·1, and the highest, 30·6; of 22 samples of Swedish butter the lowest volatile fatty acid value was 26·9, and the highest, 29·4; of 3 samples of Holstein butter the lowest was 27·3, the highest, 29·1; finally, of 7 samples of butter made by the Aylesbury Dairy Company, Limited, the lowest value was 27·6, the highest, 29·2. Of the history of all these just enumerated, the author knew nothing, with the exception of those made by the Aylesbury Dairy Company. Further, 35 samples of milk were churned under the author's supervision, and the butter fat analysed. The vast majority showed a normal composition, and only two samples analysed had a less value than 25. From one farm, however, one belonging to the Aylesbury Dairy Company, butter was obtained from the fat of which very low fatty acid values were recorded. The cream was separated from the evening's milk, cooled, mixed with the cream of the following morning's milk, and sent up to London. After churning, the following values were found:—February 2nd, 1889 = 20·9 and 21·2; February 9th, 1889 = 21·4 and 21·2; February 15th, 1889 = 21·2 and 20·4. The herd comprised 39 Shorthorns, 16 Kerrys, and 5 Jersey cows, but several changes occurred during the period of the investigations. Experiments were made to determine whether the breed had any influence on the quality of the butter fat; secondly, the food was altered, the silage, and then the oats, being replaced by other foods; but no important influence could be traced to any of these causes.

That the butter fat of the milk of cows which have been milked for a lengthened period sometimes contains a very low proportion of volatile fatty acids has been noticed by others, and the author found that the butter fat from two cows which had calved some months, in one case nearly fourteen months, previously, contained volatile acids equal to 14 to 16 c.c. N/10 alkali. The results of the analyses of the butter fat of the whole herd, when considered in relation to the length of time after calving, do not, however, show that the abnormally low values obtained can be referred to this as the principal cause. J. W. L.

Analysis of Butter Fat by the Reichert-Wollny Method. By P. Vieth (*Chem. Centr.*, 1890, ii, 722—723; from *Milch. Zeit.*, **19**, 721—724).—In addition to the results already published (preceding abstract), the author has determined the amount of volatile fatty acids in a further number of samples of butter fat.

The butter fat, which had been sent to a number of chemists from Kiel in the summer of 1888, contained, originally, fatty acids equal to 31·6—32·1 c.c. of decinormal alkali; on September 19th, 1889, 31·8 c.c.; on December 12th, 1889, 32·2 c.c.; on April 15th, 1890, 32·0 c.c. Of 29 samples of Schleswig-Holstein butter, 6 gave results below 25 c.c., 21·7 to 24·7 c.c.; these samples are of butter made at the time when most of the cows of Schleswig-Holstein are nearing the end of the period of lactation. Danish butter gave 29·8, 28·8, 29·9 c.c.; 39 samples of French butter had values varying from 26·9 to 30·8 c.c.; London-made butter, made from July 30th to November 12th, 1889, gave 25·8 to 27·1 c.c., and from March 25th to June 24th, 1890, 27·2 to 30 c.c. Some butter prepared by the author gave volatile fatty acids equal to 28·5 to 28·6 c.c. 55 samples of butter, made from milk obtained from the farms of the Aylesbury Dairy Company, the evening's milk being mixed with the following morning's milk, and then the cream separated, showed that during the months of February and March in 1889, and again in 1890, the proportion of volatile acids was abnormally low; the amount rose in April to 25 c.c., and stood above that amount during May and June. Similarly low figures were obtained in 1888. From June 11th, 1889, to June 30th, 1890, the figures varied from 21·3 to 26·2 c.c. The author cannot, however, offer any satisfactory explanation for the differences observed. J. W. L.

Marchand's Method for Estimating Fat in Milk. By A. Sjöström (*Bied. Centr.*, **19**, 855—856).—A mixture of equal volumes of ether (sp. gr. = 0·723) and pure alcohol (free from aldehyde) of 91—92 per cent. is used. 10 c.c. of milk is violently shaken in the lactobutyrometer-tube with 20 c.c. of the ether alcohol mixture, kept for a few minutes in a water-bath heated at 45°, again shaken until no more large pieces of caseïn are to be seen, and then heated for 12—15 minutes until the liquid has separated into three layers. The tube is now taken out of the water-bath, left for half an hour, and the volume of the layer of ether and fat read; the number of c.c. multiplied by 2·34 and added to 1·08 gives the percentage amount of fat by weight. A table given in the original paper (*Tidskr. f. landtmän*, **11**, 552—556) shows the amounts of fat from 0·30 c.c. (= 1·78 per cent.) to 1·38 c.c. (= 4·31 per cent. of fat). For amounts outside these limits the method is of no use. N. H. J. M.

A New Method for the Estimation of Butter Fat in Milk. By S. M. Babcock (*Chem. Centr.*, 1890, ii, 723; from *Bull. Agric. Stat. Univ. Wisconsin*, 1890, **24**).—17·5 c.c. of milk is measured into a long-necked flask of 45 c.c. capacity. The pipette employed is graduated at 17·6 c.c., an allowance of 0·1 c.c. being made for the amount of milk adhering to the sides. This amount of milk weighs 18 grams. The neck of the flask is graduated into ten parts, each such division being again subdivided into five divisions each measuring 0·4 c.c., and each principal division representing 1 per cent. of fat. To the 17·5 c.c. of milk an equal volume of concentrated sulphuric acid is added and gently mixed with the milk. The mixture is then allowed to remain at rest a short time, and placed in a centrifugal apparatus at a temperature of 93·3°; hot water is next added until the fat rises to the neck, when it is again subjected to centrifugal force. Hot water is now finally added until the fat rises to the seventh division, and the volume is then read off. In the case of condensed milk, 8 grams is mixed with 10 c.c. of water, and the sulphuric acid added. Of cheese, 5 grams is treated with 18 c.c. of water, the same quantity of sulphuric acid being added. The following results are appended.

	Babcock.	Gravimetric.	
Cream cheese	57·05	56·80	per cent. fat.
Condensed milk	9·65	9·47	,,
Common cheese	34·87	35·46	,,
,, ,, ...	33·73	33·77	,,

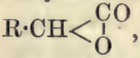
J. W. L.

Analysis of Fats. By J. Lewkowitsch (*J. Soc. Chem. Ind.*, **9**, 842—848).—After reviewing the methods at present employed in the analysis of fats, the author enters on the original part of his paper, which has special reference to the examination of the fatty acids. He examined the fat extracted from the Sawarri nuts, and obtained the following figures:—

Hehner's value	96·9 per cent. (insoluble acids).
Reichert's value	0·65 per cent. (soluble acids).
Köttstorffer's value	199·51
Mean molecular weight of the insoluble acids	272·82

Free acids (mol. weight 272·8)	2·4 per cent.
Glycerol	9·1 ,,
Iodine value of the fatty acids	51·5 ,,

The low Reichert's value and the high Hehner's value show that the amount of volatile soluble acids may be neglected. The mean molecular weight seems to point to the presence of oleïc, palmitic, and stearic acids only. In order to resolve the insoluble fatty acids into their components, they were transformed into the corresponding lead salts and extracted repeatedly with ether. The results being unsatisfactory, it was attempted, by fractional crystallisation of the acids yielding the insoluble lead salts, to concentrate the unsaturated acid into one fraction, for which purpose the lead salts were decomposed with sulphuric acid and repeatedly boiled with slightly acidified water. The free acids were dissolved in alcohol and yielded seven consecutive crystallisations, the filtrate from the last crystallisation was freed from alcohol by evaporation and yielded an eighth quantity of acids, the iodine value of which showed that the unsaturated acid had accumulated in the final fraction. The iodine values of the other fractions point to the explanation that the first portion is nearly pure palmitic acid, which, in the higher fractions, is being partly replaced by stearic acid. The soluble lead salts were decomposed in the same way, the liquid acids repeatedly washed and freed from the last traces of water. After having been kept for some time in a desiccator, the liquid acids assumed a pasty consistence, from which, however, it was not possible to separate the solid constituent. The chemical and physical properties of the acids proved that, besides the supposed oleïc acid, one or more other acids were present. The acids were, therefore, subjected to oxidation with permanganate according to Hazura's directions, and the potassium salts decomposed by sulphuric acid, when a precipitate of insoluble acids was obtained. These were extracted four times with ether. The first extract gave a gelatinous substance saponifiable by alcoholic potash. The fatty acid obtained therefrom gave an acid value of 182·5, corresponding with a molecular weight of 305. The substance, therefore, seems to be an inner anhydride of a hydroxylated fatty acid of the general formula



$R\cdot CH<\begin{matrix}CO\\ |\\ O\end{matrix}$, pointing to the existence of an acid of the formula $R\cdot CH(OH)\cdot COOH$. The second, third, and fourth extracts consisted of small quantities of the acids which are not altogether insoluble in ether, and were later on added to the main portion. The bulk of the acids was repeatedly boiled out with water without, however, losing in weight, whereby the absence of linusic and isolinusic acids was proved. On repeatedly crystallising from alcohol, it was found that only one acid was present, all fractions yielding an acid melting between 125° and 130°. The last filtrate yielded, on evaporation, an acid melting between 117° and 119°, whereby the absence of sativic and isotrihydroxystearic acids was established. The oxidised acid was then recrystallised from alcohol, and the crystals, showing every sign of purity, and melting between 132° and 133°, gave, on analysis, numbers agreeing with the formula for dihydroxystearic acid, $C_{18}H_{34}(OH)_2O_2$.

The acids soluble in water were obtained by neutralising the sulphuric acid after the dihydroxystearic acid had been filtered off, and boiling the solution down until potassium sulphate began to separate. The solution was then acidified and the bibasic acid extracted with ether. After repeated crystallisation from water, an acid was obtained melting between 126° and 130°, which proved to be a mixture of azelaic and suberic acids.

In conclusion, the author refers to his criticisms on Benedikt's acetyl values (Proc., 1890, 72 and 91). Benedikt, in his reply, declared the author's results to be wrong, and assumed that impure acetic anhydride had been used and that the fatty acids had not been washed free from acetic anhydride before titration. The author refutes Benedikt's alleged explanation for his supposed error, and in a somewhat lengthy discussion gives further proof in support of his views. D. B.

Methods of Estimation of the Fatty Substances in Vegetable Organisms. By W. MAXWELL (*Amer. Chem. J.*, **13**, 13—16).—Experiments with *Gossyppium* (cotton seed) show that not only are the lecithins not wholly separated by treatment with ether, but that even the greater proportion of these substances resists the action of ether, and can be separated only by subsequent treatment with alcohol. In the case of cotton seed, the proportion of lecithins in the total fatty substances is very small; yet more than 50 per cent. of the substituted glycerides remain in the material after extraction with ether for 15 hours. In some other varieties of seeds, such as the legumes, the total ethereal and alcoholic extracts of the seeds (which seeds contain from 2·5 to 4 per cent. of fatty substances) are composed of lecithins to the extent of 25—45 per cent. If as much as 50 per cent. of the lecithins remain unseparated after treatment of the materials with ether only, it follows, therefore, that when ether only is used as an extractive agent, from 20 to 25 per cent. of fatty substances remain undetermined in those seeds in which the fatty substances consist largely of lecithins. G. T. M.

Estimation of Morphine in Opium. By E. DIETERICH (*Zeit. anal. Chem.*, **30**, 105—107; from *Pharm. Centralhalle*, **31**, 591).—6 grams of the finely-powdered opium is rubbed up with 6 c.c. of water, rinsed into a tared flask, made up with water to a total weight of 54 grams, shaken for 15 minutes, and poured on to a ribbed filter of 10 cm. diameter. 42 grams of the filtrate is mixed with 2 c.c. of dilute ammonia (17 grams of concentrated ammonia to 83 grams of water), avoiding shaking, and the mixture is immediately poured through a ribbed filter. 36 grams of this filtrate is then mixed, in an accurately weighed flask, with 10 grams of ethyl acetate and 4 grams of the above dilute ammonia, and, after corking the flask, it is shaken vigorously for 10 minutes. Another 10 grams of the ether is added, and the ethereal layer is poured off as closely as possible; this is repeated a second time. The liquid is then poured through a plain, 8 cm. filter, and flask and filter are twice rinsed with 5 grams of water saturated with acetic ether. After thorough draining and drying at 100°, the contents of the filter are added to those of the flask, and the drying is completed. M. J. S.

Estimation of Colchicine in Colchicum Seeds. By KREMEL (*Zeit. anal. Chem.*, **29**, 727; from *Pharm. Post*, **20**, 38).—20 grams of the seeds is extracted in a percolation apparatus with 90 per cent. alcohol. The tincture is mixed with 25 c.c. of water and evaporated on the water-bath. The aqueous residue is filtered, and then four times shaken with 10—15 c.c. of chloroform. The residue from evaporating the chloroform is dissolved in water, filtered, and again extracted with chloroform. The residue from the second chloroform solution is heated on the water-bath with a few c.c. of water to decompose a compound of colchicine with chloroform, then evaporated, and finally dried over sulphuric acid to a constant weight. M. J. S.

Examination of Brewers' Pitch. By Z. v. MILKOWSKI (*Zeit. anal. Chem.*, **29**, 570—576).—About a gram of the pitch is hydrolysed with alcoholic potash, evaporated to dryness, and taken up with water. The solution is treated with ether for the removal of neutral resins, which are dried and weighed. The soap is now treated with dilute hydrochloric acid, whereupon resin and fatty acids are precipitated. The precipitate is dissolved in ether, and the ethereal solution washed with water, then evaporated and dried at 100°. The residue is dissolved in 15—20 c.c. of alcohol, treated with excess of potash, evaporated to about 5 c.c., diluted with water, and precipitated with silver nitrate. The silver precipitate is either dried and then extracted in a Soxhlet's apparatus with ether, or the extraction may be performed with the precipitate still suspended in the aqueous liquid. Resin, with traces of silver salts, pass into the ether solution. The silver is removed by hydrochloric acid and the filtered ethereal solution evaporated for the resin. The undissolved silver salt is decomposed by acid, and the liberated fatty acids dissolved in ether, and weighed after evaporation. Special apparatus, modified from that of Schwarz (*Zeit. anal. Chem.*, **23**, 368), for the extraction with ether, is figured. The average composition of the pitch is:—Neutral resin, 11·52; resin, 74·86; and fatty oil, 13·42 per cent.

M. J. S.

Estimation of Urea. By S. H. SMITH (*Pharm. J. Trans.* [3], **21**, 294).—For the estimation of urea, exactly 5 c.c. of the urine is introduced into an Allen's nitrometer which has been filled with a strong solution of common salt. About 8 c.c. of solution of sodium hypobromite is then added. The latter is to be freshly prepared by adding 1 c.c. of bromine for every 10 c.c. of a stock solution in which 200 grams of sodium hydroxide is dissolved in 500 c.c. of water. Each c.c. of nitrogen evolved from 5 c.c. of urine represents 0·0539 per cent. of urea. R. R.

General and Physical Chemistry.

Measurement of Refractive Indices at High Temperatures by means of the Total Reflectometer. By J. W. Brühl (*Ber.*, **24**, 286—296).—A description of a method of measuring refractive indices at high temperatures by the aid of Pulfrich's refractometer.

H. C.

Explanation of Optical Activity. By A. Fock (*Ber.*, **24**, 101—111).—Landolt divides optically active substances into three classes: those which rotate polarised light only when in the crystalline form; those which rotate it only in solution or when fused, that is to say, in the amorphous state, and, lastly, those which in both conditions show optical activity. Only one substance, strychnine sulphate, has hitherto been discovered belonging to the last class. The optical activity of crystals is generally explained by assuming for these a screw-shaped structure: that of liquids is referred to the nature of the chemical molecule and, more particularly, to the presence of an asymmetrical carbon atom.

The author does not regard the explanation of the optical activity of crystals usually given as satisfactory. It is not probable, and is not consistent with what is known of the symmetry of crystals. That the laws of circular polarisation are the same for both the crystalline and amorphous states, would also lead to the conclusion that the same explanation would hold in both cases. A key to this explanation may be sought in the fact that substances which are optically active when amorphous, crystallise in hemihedral forms. According to Sohncke, hemihedrism may be explained by assuming a certain polarity in the molecules building up the crystal. The author shows, reasoning from the fact that the molecule of an optically active substance contains an asymmetrical carbon atom, that circular polarisation may be explained by assuming that the axis of polarity of the molecule coincides with its axis of rotation and with the direction which offers greatest and least resistance, according to the orientation of the molecule, to the passage of a ray of light. H. C.

Relation between Electrical and Chemical Energy in Galvanic Cells. By E. Lévay (*Ann. Phys. Chem.* [2], **47**, 103—114).—The object of these experiments was to determine for certain galvanic cells the heat generated chemically and the heat equivalent of the current, and to obtain an exact measure of the difference between the two. The heat evolved in the cell was determined calorimetrically, and that of the circuit was determined in like manner by means of a silver voltameter placed within the calorimeter along with the cell. Two cells were examined, the Daniell and the De la Rue, three determinations being made with each. With the Daniell, the heat equivalent of the current is greater than that generated chemically, so that the cell works with absorption of heat. The reverse is true of the De la Rue cell; but in this case the relative amount of electrical energy increases with the concentration of the solution in the cell. The results are compared with those formerly obtained by Jahn, with which they show a close agreement. H. C.

Variations of Electromotive Force of Cells of Certain Metals, Platinum, and Nitric Acid. By G. J. Burch and V. H. Veley (*Proc. Roy. Soc.*, **48**, 460).—When copper, silver, bismuth, and mercury are introduced into purified nitric acid of different degrees of concentration, and a couple made with platinum, the E.M.F. of the cell increases considerably until it reaches a constant, mostly maximum, value. The rise of E.M.F. is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former alone, although any impurity affects the result to a remarkable degree. If nitrous acid has been previously added to the nitric acid, the maximum E.M.F. is reached at once.

If the conditions favour a more rapid solution of the metal, and, consequently, a more rapid production of nitrous acid, then the rise of E.M.F. is concomitantly more rapid. If any substance is added which would tend to destroy the nitrous acid as fast as it might be formed (for example, carbamide), then the rise of E.M.F. is extremely slow. J. W.

Electromotive Force of Galvanic Elements. By A. Oberbeck and J. Edler (*Ann. Phys. Chem.* [2], **42**, 209—226).—After giving a short account of the theoretical investigations on the E.M.F. of voltaic combinations, the authors proceed to describe their own experiments on non-reversible elements. They measured the E.M.F. of amalgams of zinc, cadmium, tin, lead, and bismuth against pure mercury in different salt solutions, using the compensation method and a mirror galvanometer. The amalgams, which, as far as polarisation is concerned, behave like the metals themselves, were prepared electrolytically, except in the case of bismuth.

From experiments with numerous solutions of sulphates, chlorides, bromides, iodides, &c., it appeared that the E.M.F., besides depending on the two metals which form the electrodes, is also dependent on the negative component of the salt solution: the metal of the salt only exerts an influence when it is the same as one of the electrodes, in which case the E.M.F. is diminished.

When the metals are arranged according to the magnitude of the E.M.F., they always follow each other in the same order (that, namely, in which they are given above), no matter what the salt or acid solution may be. In alkaline solution, the values for lead and tin are abnormally high. The authors finally indicate a connection between the E.M.F. and the heat of formation of certain salt solutions as determined by Thomsen. J. W.

Chemistry of the Accumulator. By M. Cantor (*Monatsh.*, **9**, 433—451).—The charging and discharging of a secondary cell are accompanied by a chemical change in the electrodes and the electrolyte, and by an evolution of gas. In order to ascertain what chemical changes take place, it would be necessary to analyse the electrodes and electrolyte both before and after charging, and to collect and examine the gases given off. The latter, which consist of oxygen and hydrogen, would only require collecting separately and measuring. The change in the electrolyte is also readily ascertained, but that of the electrodes presents some difficulty. It may, however, be determined indirectly by charging each plate of the cell separately, using as the second pole an electrode the chemical composition of which remains unaffected. In such a combination, the change in the electrolyte is due solely to the reaction which takes place between it and the electrode and to the gas evolved. The change in the composition of the electrolyte can be determined, as also the gas evolved, and from these data the change which has taken place in the electrode is ascertained.

Applying this principle to the study of the changes that take place in the negative plate of a secondary cell, consisting of lead coated with a mixture of lead oxide and sulphate, the plate is so arranged that it forms the cathode, whilst platinum forms the anode, in a solution of sulphuric acid which is being submitted to electrolysis. Examination and measurement of the gas evolved and a determination of the change in the electrolyte gave rise to the following results:—The lead oxide contained in the plate is first converted into sulphate. The hydrogen, which is formed electrolytically, reduces the lead sulphate with the formation of sulphuric acid and metallic lead. The freshly reduced lead decomposes the sulphuric acid with evolution of hydrogen and the formation of lead sulphate. These two reciprocal processes continue until a condition of equilibrium is reached, when the cell is charged. It is to the local action, between freshly reduced lead and sulphuric acid, that those phenomena are due which led Streintz (Abstr., 1890, 315) and others to conclude that lead in accumulators has the power of occluding hydrogen, which, however, is not the case. H. C.

Electrical Resistance of Bismuth. By G. H. ZAHN (*Ann. Phys. Chem.* [2], **42**, 351—352).—The author confirms Lenard's observation that the electrical resistance of metallic bismuth is slightly less (about 0·12 per cent.) when measured with an alternating current than with a constant current. J. W.

Conduction of Electricity by the Vapours of Heated Salts. By S. ARRHENIUS (*Ann. Phys. Chem.* [2], **47**, 18—76).—The spray from different salt solutions was introduced through the air holes of a Bunsen burner into the flame, and the alteration in the resistance between two platinum plates placed in the flame caused by the introduction of the salt was observed. From careful estimations, the proportional amount of the salt vapour present in the hot gases, or what the author terms the dilution of the salt vapour, could in each case be determined.

Salts of the alkali metals were first examined. It was found that the salts of each metal had a conductivity which was quite independent of the nature of the negative radicle, salts of one and the same metal having all approximately the same conductivity for equal degrees of dilution. This law holds more particularly when the dilution is large, the individuality of each salt being somewhat more marked when present in a concentrated state, especially in the case of the sodium salts. As far as there is any difference among the haloïd salts, the iodides conduct better than the bromides, and the bromides better than the chlorides. The greater the atomic weight of the metal, the better do its salts conduct. The conductivity changes with the dilution so that it is always proportional to the square root of the concentration, except in the case of great dilutions when the increase in conductivity is somewhat greater, and for very small dilutions when the increase is somewhat less than that calculated from the square root of the concentration. The conductivity of hydrogen and ammonium salts is practically *nil.*

Whereas in the case of the alkali metals the flame immediately takes the conductivity characteristic of the salt introduced, this is not the case with salts of the metals of the alkaline earths; as on introducing one of these into the flame, the conductivity increases slowly until it reaches a maximum. The effect of the salt on the conductivity also does not immediately disappear when the supply of salt to the flame is stopped, but its influence remains perceptible for many hours, and can in fact only be finally removed by washing the electrodes in hydrochloric acid. The latter seem to become coated with the oxide or sulphide of the metal (hydrogen sulphide being sometimes given off on washing the plates in acid), and the presence of these as solid particles in the flame serves to bring about a conductivity perfectly independent of that of the salts themselves. For this reason, regularities similar to those noticed in the case of the salts of the alkali metals cannot be observed. It is found, however, that a maximum conductivity is reached most rapidly, the higher the atomic weight of the metal and the more concentrated the salt. The conductivity also seemingly increases with the atomic weight.

The salts of a large number of other metals were examined, but of these only silver and lead nitrates were found to have an appreciable conductivity in the Bunsen flame. Experiments with mixtures of potassium and sodium sulphates and chlorides led to the interesting result that the mixed salts behave as electrolytes having a common ion. Hence it was possible to calculate, within the limits of experimental error, the conductivities of such mixtures from those of the salts composing them, in accordance with the principles laid down by the author (Abstr., 1890, 437).

It would seem that the conductivity of salt vapours in the Bunsen flame may be of two kinds, firstly, that of the solid particles which may be formed by decomposition of the salt; and, secondly, that due to the salt itself. The latter the author regards as being electrolytic in its nature. The conductivity takes place in accordance with Ohm's law for an E.M.F. not greater than 0·2 volt, but above this E.M.F. Ohm's law no longer holds. The fact that the salts of any alkali metal all have the same conductivity is readily explained if it is assumed that the salts at the temperature of the flame, about 1200°, undergo dissociation. In the presence of the large amount of water vapour which the flame contains, the metal would then be converted into hydroxide and the acid set free. Since the latter has no conductivity, the former alone would in all cases be active, and hence the conductivity of the salts of any alkali metal would always be the same, namely that of the hydroxide. The author discusses the change of conductivity with concentration, regarding the conductivity as electrolytic, and applying those laws which have already been established for aqueous solutions. The agreement between the theoretical deductions and the experimental results he considers establishes the correctness of his assumption, and also of those gaseous laws which have been derived from the study of dilute solutions. H. C.

Conductivity of Isomeric Organic Acids and their Salts. By W. Ostwald and by D. Berthelot (*Compt. rend.*, **112**, 229—231).—Ostwald claims priority in the determination of the electrical conductivities of isomeric acids, and in the discovery of the fact that tartaric acid and racemic acid have the same conductivities, which he regards as proof of the complete dissociation of the latter in dilute solution.

D. Berthelot replies that the application of measurements of electrical conductivity to the study of chemical problems is mainly due to Kohlrausch, Bouty, and Foussereau; that his method (this vol., p. 375) is different from that used by Ostwald; and that he has investigated the behaviour of mixtures, whilst Ostwald confined himself to the study of single electrolytes. The dissociation of racemic acid in solution had already been established by the thermochemical measurements of Berthelot and Jungfleisch. C. H. B.

Electrical Behaviour of Precipitated Membranes. By A. Oberbeck (*Ann. Phys. Chem.* [2], **42**, 193—208).—Two tubes closed at the bottom with parchment paper were filled with solution of zinc or copper salt, and immersed in a beaker containing a salt solution of such nature as to give a precipitate with either the metal or the acid radicle of the first salt. The precipitate is formed within the parchment paper, and exhibits electrical properties comparable to those of a metallic plate in the same position (compare Ostwald, Abstr., 1890, 1354; Tammann, this vol., p. 140). The object of the author was to measure the polarisation caused by the introduction of such membranes into an electrolytic circuit. For this purpose, he introduced into the two tubes, as electrodes, rods of amalgamated zinc when a zinc salt was employed, and of copper when a copper salt was used. These electrodes are practically unpolarisable by the primary current, so that any polarisation observed must have its seat in the precipitated membranes. When the polarisation of these was measured separately, it was found only at that membrane where the precipitate was thickened by the action of the current. For instance, with copper sulphate in the two tubes and potassium ferrocyanide in the beaker, the ion FeC_6N_6 travels to the tube containing the anode, and consequently strengthens the membrane by meeting the copper ion there; the potassium ion, on the other hand, meets the ion SO_4 in the membrane at the cathode, and no precipitate is formed. Such a membrane, then, as copper ferrocyanide the author calls an anodic membrane; the lead sulphate formed at the tube containing the negative electrode when the beaker is filled with a solution of a lead salt he calls a cathodic membrane.

Copper salts with potassium ferrocyanide, or ferricyanide, give an E.M.F. of polarisation rising to a maximum of about 1 volt. The primary current becomes much weaker as it flows, owing to the thickening of the membrane and the increasing resistance. Porous clay cells in place of the parchment paper offer much less resistance, so that the E.M.F. of polarisation with them is greater, corresponding with the increased current density. Zinc salts give a polarisation only about half that of copper salts. The polarisation here depends on the cation.

With lead solution in the beaker, the polarisation is as much as 2 volts. Spongy lead separates at the cathodic membrane, and the current increases, probably in consequence of this. The E.M.F. of calcium, strontium, and barium chloride against zinc sulphate is equal to 0·08, 0·39, and 0·73 volt respectively. Silver nitrate gives a polarisation of −0·26 volt against copper sulphate, and −0·24 volt against zinc sulphate.

The author finds no characteristic difference between permeable and impermeable membranes when long continued currents are employed. The opposite result found by Tammann he considers as due to the rapidly alternating currents used by the latter. J. W.

Relation between Atomic Weight and Magnetism. By L. ERRERA (*Ber.*, **24**, 88—89).—The author maintains the impossibility in the present state of our knowledge of the subject of establishing any more definite relation between the magnetism and the atomic weights of the elements than that which he has formerly pointed out, namely, that the elements in the odd series in Mendeléeff's table are diamagnetic, and those in the even series paramagnetic. He criticises a paper by Bachmetieff (*J. Russ. Chem. Soc.*, **21**, 39) dealing with this question, in which he points out several errors. H. C.

Thermal Dilatation of Liquid Bismuth near its Melting Point. By G. VICENTINI (*Rend. Acad. Lincei*, **6**, ii, 121—125 and 147—152).—The following constants were previously obtained by the author, using large dilatometers (*Atti Real. Acad. Torino*, **22** and **23**):—Sp. gr. of bismuth at 0°/4° = 9·787; m. p. = 271°; sp. gr. of solid bismuth at its melting point = 9·673; sp. gr. of molten bismuth at the melting point = 10·004; decrease in density on passing from the liquid to the solid state = 3·31 per cent.; mean coefficient of dilatation between its m. p. and 300° = 0·000120. From his observations, the author also concluded that liquid bismuth has its maximum density at its melting point. Lüdeking (Abstr., 1888, 790), using small thermometers with capillary stems as dilatometers, found a different set of constants, and attributed the discrepancies to the presence of air in the author's large dilatometers. This is now denied by the author, who declares that Lüdeking's results are untrustworthy, on account of the uncertainty in the indications of the variation of the volume of the metal in the bulb, as shown by the column of bismuth in the capillary stem at temperatures close to the solidifying point, more especially as Lüdeking's use of a mercury-bath involved the exposure of a portion of the stem, which would, consequently, be at a slightly lower temperature than the bulb. The author found it necessary to adopt special precautions to secure the proportionate movement of the bismuth columns in his wide tubes, even when entirely immersed in a paraffin-bath. The slight expansion of the metal just before solidification from which Lüdeking inferred the existence of a point of maximum density, really takes place at a temperature at which, if maintained constant, bismuth slowly solidifies, and is due to a partial solidification. Lüdeking's metal, it is also stated, was contaminated with mercury.

The author has now made a series of experiments by the hydrostatic method, using a bath of purified petroleum residues, and cylindrical glass vessels containing 9 to 12 c.c. of bismuth. The results obtained confirm those of the previous experiments, and show that within the limits of sensibility of the apparatus, about 1/110,000, the volume of liquid bismuth gradually decreases when cooled from 281° to its melting point (271·5°) and even a little below (270°). The sp. gr. of liquid bismuth at its melting point is now found to be 10·064, the increase in volume in passing from the liquid to the solid state 3·39 per cent., and the mean coefficient of dilatation between its melting point and 280° 0·000306. S. B. A. A.

Determinations of the Heat of Capacity and Heat of Fusion of some Substances to Test the Validity of Person's Absolute Zero. By S. U. PICKERING (*Proc. Roy. Soc.*, **49**, 11).—Person made determinations with eight substances to show that the temperature at which their heat of fusion became *nil*, $t - \frac{l}{C - c}$ (t = temperature of fusion, l = heat of fusion at $t°$, C = heat capacity of liquid, c = heat capacity of solid), was −160° in all cases. This he called the absolute zero. His conclusions may for several reasons be questioned, the chief reason being that he determined C and c at any temperature which happened to be most convenient, and the value of these is largely dependent on temperature; they should both refer to the same temperature, and this is necessarily $t°$. The author deduces this value for C and c at $t°$ from the determinations made at a series of different temperatures. The substances examined were, sulphuric acid and its monohydrate, hydrated calcium nitrate, and naphthalene, and their temperatures of no crystallisation were found to be −369°, −177°, −234°, and −214° respectively, thus refuting Person's conclusion. Water gives −167° when the values for C and c at 0° are taken. Benzene was also examined, but the heat capacity of the solid was found to be greater than that of the liquid. This is probably due to an incipient fusion occurring below the temperature of true fusion.

The following are the values given for C, c, and l per gram at the respective fusing points, t:—

	C.	c.	l.	t.
H_2SO_4	0·3355	0 2721	24·031	10·352°
H_2SO_4,H_2O	0·4430	0·2273	39·918	8·53°
$Ca(NO_3)_2,4H_2O$ ..	0·5185	0·3973	33·493	42·4°
$C_{10}H_8$	0·4824	0·3612	35·625	79·86°
C_6H_6	0·3957	0·4600	29·433	5·41°
H_2O	1·0	0·5243	79·25	0·0°

S. U. P.

Use of the Calorimetric Bomb for the Determination of the Heat of Combustion of Coal. By SCHEURER-KESTNER (*Compt. rend.*, **112**, 233—236).—Berthelot's calorimetric bomb answers well for the determination of the heat of combustion of coal, but for accurate estimation, it is necessary to determine the percentage of sulphur in order to make the necessary correction after determining the acidity of the products. For practical purposes, this last correction may be omitted, since the heat of conversion of the nitrogen into nitric acid is practically the same as the heat of combustion of the carbon; and sulphur increases the heat of combustion in the furnace as well as in the bomb. The difficulty of determining the amount of ash is obviated by converting the powdered coal into pastilles as recommended by Berthelot. The results obtained are lower than those obtained 20 years ago by the author and Meunier Dollfus, a result partly due to a better knowledge of the corrections required, and they are also lower than those obtained with Favre and Silbermann's calorimeter. The corrected determinations reduce the number of coals with heats of combustion higher than those calculated from their elementary composition. and it is possible that coals exist with heats of combustion actually lower than those calculated by Dulong's formula. C. H. B.

Dalton's Law. By M. MARGULES (*Ann. Phys. Chem.* [2], **42**, 348—350).—The author draws attention to the difference between the results calculated by him (*Wiener Ber.*, **98**, 883) and by Galitzine (this vol., p. 378) for the pressure of compressed gases, and attributes them to the employment by the latter of an unsatisfactory formula given by Sarrau (Abstr., 1882, 686) for nitrogen. J. W.

Determination of the Specific Gravity of Viscid Substances. By J. W. BRÜHL (*Ber.*, **24**, 182—183).—The apparatus consists of a graduated flask; the neck is 2 mm. in diameter, and has a side tube at the upper end. A quantity of the substance under examination is first introduced into a pipette by the help of an air pump, the delivery tube of the pipette, which is long enough to reach to the bottom of the flask, is inserted in the neck of the flask, the connection between the neck of the flask and the pipette being made air-tight with a small piece of rubber tubing; on exhausting the flask by means of the side tube, the liquid flows out of the pipette. A flask with a capacity of 10 c.c. gives results which are stated to be accurate to four places of decimals. J. B. T.

Determination of the Specific Gravity of Viscid Substances. By C. SCHEIBLER (*Ber.*, **24**, 357—358).—J. W. Brühl has described a method of determining the specific gravities of viscid substances (preceding abstract). The author draws attention to the fact that 12 years ago he described a method for determining the specific gravity of beet-molasses which is simpler and more accurate than that of Brühl, and is applicable to all liquids.

A pipette is used closed at both ends with glass taps, to which glass tubes are fitted by grinding. The capacity is determined once for all for a certain temperature; the pipette is then filled by sucking up the liquid whose specific weight is required, the bottom tap shut, the tube attached to it removed, and the whole put into a beaker containing water at the required temperature. The top tap is then closed, its tube removed, the outside of the apparatus wiped clean and dried, and the apparatus weighed. The advantages of the method are that it is applicable to all liquid substances, that the specific gravity can be determined at any required temperature, and that any convenient size of apparatus can be employed. E. C. R.

Hypothesis of Electrolytic Dissociation. By S. ARRHENIUS (*Ber.*, **24**, 224—231).—A reply to the criticisms of Traube (this vol., p. 255). According to the dissociation hypothesis, a salt in aqueous solution is dissociated into its ions, these latter being charged positively and negatively respectively. In any homogeneous solution, the ions exist perfectly free side by side, and owing to their freedom of motion they so intermingle that the homogeneity of the solution is never disturbed. But if the solution is not homogeneous, and varies in concentration, diffusion of the salt will take place from the more concentrated to the less concentrated portion. Since one of the ions will move more rapidly than the other, a larger number of these ions will pass into the less concentrated portion of the solution than of the others. This will cause this portion of the solution to take the charge of these ions, and the other portion that of those remaining. A certain tension will thus after a time be established, and a state of equilibrium result in which equal diffusion of both ions may be said to take place in unit of time. Electrolytic dissociation differs, therefore, from ordinary dissociation, as Traube asserts; but in the case of homogeneous solutions, both kinds of dissociation exhibit the same properties.

The dissociation hypothesis does not demand that *all* properties of dilute solutions shall be of additive nature. In cases, however, in which additive properties in solution may be predicted, these have always been found. This is illustrated by the specific conductivity and specific resistance of water. The first should, according to the hypothesis, be proportional to the amount of the dissolved salt, and this is found to be the case; for the second, the hypothesis makes no such prediction, and in practice it is not found to be the case. That the colour of any particular ion in solution should be the same is correct, but in the instances given by Traube, the ions are in every case different.

That the dissociation hypothesis stands altogether in contradiction to the hydrate theory, the author denies, having himself pointed out the possibility of the existence of molecular aggregates in concentrated solutions. The hydrate theory has, however, altogether failed to give any explanation of the properties of dilute solution, to which the dissociation hypothesis has been so successfully applied, and even in other cases there is disagreement between the supporters of the hydrate theory themselves (see Pickering, Abstr., 1890, 857).

Ostwald's application of the gaseous laws to electrolytic dissociation has led to the establishment of a formula which has been successfully tested in the case of a large number of acids. Exceptions have been found to the formula, but sufficient data do not exist at present to serve for the discussion of these. That heat is developed in some cases of electrolytic dissociation finds a parallel in the case of the development of heat attending the formation of oxygen (3 mols.) from ozone (2 mols.).

The author also points out that some of the statements made by Traube are erroneous, and that in calculating the values of *i* from the freezing point determinations and electrical conductivity, precautions were taken to make the numbers obtained from each strictly comparable. H. C.

Nature of Osmotic Pressure. By R. NASINI (*Rend. Acad. Lincei*, **6**, i, 175—182).—In this paper, Pfeffer's experiments, and the extent to which they may be considered as the experimental basis of Van't Hoff's formula $PV = Rt$, are discussed at great length. The author arrives at the conclusion that the results obtained with the cells hitherto constructed afford but little support to the theory, the expression of which in the form of Van't Hoff's formula he regards as a convenient method of implicitly assuming the identity of matter in the state of a gas and of a dilute solution, without premising conditions of temperature and pressure at which the existence of a solution might be impossible. This assumption, which has been explicitly made by Planck (Abstr., 1888, 895) and by J. J. Thomson, may rather be regarded as having a measure of physical explanation in the osmotic phenomena hitherto observed. S. B. A. A.

Velocity of Decomposition of Nitrous Acid in Aqueous Solution. By C. MONTEMARTINI (*Rend. Acad. Lincei*, **6**, ii, 263—270). —The solutions obtained by decomposing solutions of silver nitrite with dilute hydrochloric acid were allowed to remain, and the free nitrous acid determined at intervals by titration with potassium permanganate. The rate of decomposition may, in general, be represented by the formula $-dC/dT = kC$, or $k = 1/T \log C_0/C$ (T being the time in hours and C the concentration in grams per 100 c.c. of solution). k is, however, only constant between certain limits of concentration, and varies with the temperature. The decomposition of nitrous acid in solution is a true dissociation phenomenon which may be represented by the equation $3HNO_2 = 2NO + HNO_3 + H_2O$, and it accordingly depends on the vapour tension of the nitric oxide evolved. When the action is allowed to proceed in a current of carbonic anhydride, the theoretical amount of nitric acid is always found in the solution; in presence of air, however, the nitrogen tetroxide formed partially redissolves and increases the amount of nitric acid. The reaction may, to a certain extent, be reversed by passing a current of nitric oxide into a solution of 4 grams of nitric acid in

200 c.c. of water for about an hour, the experiment being performed in an atmosphere of carbonic anhydride, and a current of carbonic anhydride finally passed through the solution to remove any dissolved nitric oxide; the nitric acid was found to contain 0·1139 gram of nitrous acid. Solutions of nitrous acid allowed to remain in sealed tubes cease to decompose as soon as the vapour tension of the evolved nitric oxide is sufficiently great. Solutions of silver or potassium nitrite remain practically unaltered after two months' exposure to diffused light. S. B. A. A.

Unit of Atomic Weights. By W. A. NOYES (*Ber.*, **24**, 238—240).—The author points out that the determinations of the combining ratio of oxygen and hydrogen which have been carried out within the last twenty years have, with one exception, all given numbers for the atomic weight of oxygen which are less than 15·90. If 15·89 be accepted as the most probable number for the atomic weight of oxygen, and the other atomic weights are calculated on this basis, the majority of the elements, particularly of the more common elements, will be found to have atomic weights which differ very largely from whole numbers. If, on the other hand, the atomic weight of oxygen is fixed as 16 (Brauner, Abstr., 1889, 335) only six elements, Na, S, K, Ag, I, and Pt, are found to have atomic weights which differ from whole numbers (half numbers in the case of Cl, Cr, and Sr) by a larger amount than the possible error in the atomic weight itself. In this case, the atomic weight of hydrogen would be 1·007, but for all ordinary work the error introduced by employing unity in place of this number is so small that it may be neglected. The advantages of fixing O = 16 as the basis for the atomic weights of the other elements are, therefore, so obvious that the author urges its acceptance by chemists generally. H. C.

Mordants and the Periodic Law. By PRUD'HOMME (*Compt. rend.*, **112**, 236—239).—In each group of the periodic system, taking the odd and even series, there is a continuous variation in the shade of colour produced, from blue to red or red to blue, as, for example, with magnesium, zinc, and cadmium, or with calcium, strontium, and barium. Boisbaudran has shown that in groups of elements such as these or potassium, rubidium, and cæsium, the wave-lengths of corresponding lines in the spectra are proportional to the molecular weight. It would seem, therefore, that metallic oxides communicate to their combinations with colouring matters vibrations which are proportional to those of the elements which they contain. In each period, from the first to the fourth group, there is progression from blue to red; in the fifth to the eighth group the progression is from red to blue. Group 4 does not form a real maximum, since the shades of colour in this group have an excess of yellow. The orange term does not belong to Group 4, but is represented in Group 5 by vanadium. Tin, the atomic weight of which is nearly half that of uranium, represents in an especial manner yellow and orange shades. It is noteworthy that the colours of "lakes" often show progression the reverse of that obtained with the same oxides on the fabrics. The influence of the bases is perceptible in the behaviour of many salts; and the influence of the haloïds is well seen in the derivatives of fluoresceïn.

C. H. B.

Modification of the Sprengel Pump. By G. Guglielmo (*Rend. Acad. Lincei*, 6, ii, 153—155).—From the top of the Sprengel air chamber, a short tube provided with a stop-cock leads upwards into a glass globe, to the top of which a large cup or funnel is attached by a short stoppered neck. The branch tube connected with the receiver is soldered low down in the side of the air chamber and bent vertically upwards. The upper part of the fall tube is also fitted with a stop-cock. The cup and globe are filled with mercury, the stopper replaced in the cup, and all the stop-cocks opened until a moderate degree of exhaustion is reached. A good vacuum is thus formed in the globe, which effectually deaërates the mercury which is allowed to enter the globe from time to time by raising the stopper; moreover, any risk of access of air into the chamber is avoided. The pressure of the residual gas in the air chamber may be found by closing the stop-cock in the fall tube and allowing the mercury to rise in the branch tube until the volume of the gas in the air chamber is reduced to one-hundredth part of its previous volume, and then observing the difference between the levels of the mercury in the chamber and branch tube.

S. B. A. A.

Inorganic Chemistry.

Hydrogen Nitride (Azoimide). By T. Curtius and R. Radenhausen (*J. pr. Chem.* [2], **43**, 207—208; compare this vol., p. 56).—Pure hydrogen nitride is obtained by fractionally distilling the aqueous solution, the preparation of which has been already described; the first portion of the distillate is again fractionated, until, after four repetitions of the process, an acid distils over at 45°; this contains 91 per cent. of hydrogen nitride, but the composition of the distillation does not correspond with that of a definite hydrate. The complete dehydration is effected by fused calcium chloride.

Hydrogen nitride is a clear, colourless, mobile liquid; it boils without decomposition at 37°, dissolves in water and alcohol, and has the same odour as its aqueous solution (*loc. cit.*), in a more marked degree. It explodes in contact with a hot substance, and sometimes even at the temperature of the room, with a blue flash. Researches on its electric conductivity by Ostwald lead to the conclusion that it is a somewhat stronger acid than acetic acid. Attempts to determine its vapour density were frustrated by its instability; when 0·05 gram of it was passed into a barometer tube at the ordinary temperature it exploded with such violence that the tube was pulverised and, along with the mercury, scattered in all directions; on another occasion, 0·7 gram of it exploded when the tube containing it was removed from the freezing mixture, shattering all the glass in the neighbourhood and wounding one of the authors of the paper.

Mendeléeff (this vol., p. 394) has suggested that the ammonium salt of this acid would undergo an isomeric change, like ammonium cyanate; the authors have not found this to be the case. *Ammonium nitride* crystallises in large prisms which are unchanged by heating with water or by sublimation; they are not hygroscopic, and gradually evaporate when exposed to the air. A. G. B.

Conditions of Chemical Change between Nitric Acid and Certain Metals. By V. H. Veley (*Proc. Roy. Soc.*, **48**, 458—459).—Copper, mercury, and bismuth do not dissolve in 30 per cent. nitric acid at 30°, provided that nitrous acid is neither present initially nor formed subsequently. If the conditions are such that these metals dissolve, then the amount of metal dissolved and the amount of nitrous acid present are concomitant variables, provided that the nitric acid is present in considerable excess. Metallic nitrite, it would appear, is first formed, together with nitric oxide; the former is at once decomposed by the nitric acid with liberation of nitrous acid, whilst the latter reduces the nitric acid to form a further quantity of nitrous acid. Nitrous acid is invariably the initial product of reduction of the nitric acid.

Copper, mercury, and bismuth dissolve very readily in a 1 per cent. solution of nitrous acid. Under these conditions, nitric acid present in slight excess interferes with the chemical change instead of promoting it. This result is probably due to the greater stability of nitrous acid in presence of nitric acid.

Hydrogen reduces nitric to nitrous acid in presence of cupric or lead nitrate. It also converts mercuric into mercurous nitrate, but does not produce any change in solutions of bismuth or zinc nitrate dissolved in nitric acid. J. W.

Electro-metallurgy of Aluminium. By A. Minet (*Compt. rend.*, **112**, 231—233; compare Abstr., 1890, 532 and 1040, and this vol., p. 152).—The steel crucible is made smaller, and is provided with an internal lining of carbon which serves as the negative electrode. The difference of potential between the two electrodes is 4·55 volts, and the yield 31·9 grams of aluminium per horse power per hour, or 31·3 horse powers per hour for 1 kilo. of aluminium. The author believes that it will be possible to reduce the difference of potential to 4 volts, and under these conditions there will be no electrolysis of the sodium chloride, and the yield will reach 70 per cent. of the theoretical quantity. The loss of 30 per cent. is due to the action of the fused fluorides on the aluminium, and does not occur when aluminium alloys are made, since in this case the electrolytic cell is composed of the other metal, and the liberated aluminium at once combines with it. C. H. B.

Atomic Weight of Bismuth. By A. Classen (*J. pr. Chem.* [2], **43**, 133—138).—A reply to Schneider's criticisms (this vol., p. 271). Schneider's metal must have contained not only lead, but also copper, iron, and other metals. The same must be said of Marignac's metal, for even 16 fractional precipitations as basic bismuth nitrate are not sufficient to eliminate all impurities. Schneider naïvely points out that Marignac made each of his seven determinations on equal weights of his bismuth oxide under the same conditions. It is evident that any decomposition of his sulphate at the temperature to which it was exposed would not have been made apparent by these experiments. Bailey (Trans., 1887, 676) has pointed out that bismuth sulphate begins to decompose at 405—418°. A. G. B.

Auric Sulphide, Au_2S_3. By U. ANTONY and A. LUCCHESI (*Gazzetta*, **20**, 601—607).—Berzelius obtained a substance having the composition Au_2S_3, by fusing metallic gold with an excess of potassium pentasulphide. The existence of such a compound has, however, been denied by Levol, Schrötter, and latterly by Hoffmann and Krüss (Abstr., 1887, 1019; 1888, 28). As the author's experiments on aurosoauric sulphide (Abstr., 1890, 1216) showed that the action of hydrogen sulphide on gold trichloride largely depends on the temperature of the solution, attempts were made to prepare auric sulphide by the action of hydrogen sulphide at a very low temperature, but without success. On passing, however, a rapid current of perfectly dry hydrogen sulphide through a U-tube containing potassium aurochloride kept at a temperature of $-10°$ until the issuing gas was free from hydrogen chloride, a brown mass was obtained, but on attempting to separate the potassium chloride by treating this product with water at 0°, it underwent complete decomposition, hydrogen sulphide being evolved, gold precipitated, and *sulphuric acid* passing into solution. As neither aurous nor aurosoauric sulphide behaves in this manner, the experiment was repeated with lithium aurochloride, a deliquescent salt forming orange-coloured crystals which contain 2 mols. H_2O after prolonged drying in a current of air at 70°, become anhydrous when similarly treated at 90°, and begin to decompose at 100—105°. The perfectly dry hydrated salt was treated with hydrogen sulphide at $-10°$, the product freed from lithium chloride by extraction with absolute alcohol, and the residue dried in a current of nitrogen at 70°. It consisted of a black, amorphous, graphitic mass of the composition Au_2S_3, from which no trace of free sulphur could be removed by treatment with carbon bisulphide. It completely decomposes into gold and sulphur when heated to 200—205°. Auric sulphide may likewise be prepared by decomposing the dry *anhydrous* lithium aurochloride with hydrogen sulphide at the ordinary temperature. Its properties and reactions are at present under investigation.

S. B. A. A.

Mineralogical Chemistry.

Native Nickel in River Sand near Biella (Piedmont). By A. SELLA (*Compt. rend.*, **112**, 171—173).—The sand of the torrent Elvo, near Biella, contains grains which closely resemble metallic platinum, some being silvery or yellowish-white, whilst others have a steel-grey colour. They contain Fe, 26·6; Ni, 75·2 = 101·8, and agree somewhat closely in composition with the alloy Ni_3Fe. The grains are in all probability of terrestrial origin. C. H. B.

Brookite from Beura (Ossola). By G. STRUEVER (*Rend. Acad. Lincei*, **6**, i, 77—79).—The author has discovered crystals of brookite, a mineral not hitherto found in Italy, in the gneiss caves of Beura, in the district of Ossola. It occurs among lamellar crystals of calcite in blackish plates with a bright, adamantine lustre, and is accompanied by needles of dark tourmaline and scales of chlorite. The tabular faces (100) are covered with vertical striæ, owing to their alternate combination with faces of vertical prisms. The crystals are 2 mm. long, 1·5 mm. broad, and 0·25 mm. thick; they are generally opaque, but contain translucent patches which transmit dark-green light. The crystallographic measurements agree with those already given, but no chemical analysis has been made. S. B. A. A.

Rhodochrosite from Franklin Furnace, New Jersey. By P. E. BROWNING (*Amer. J. Sci.*, **40**, 375—376).—The specimen of rhodochrosite, an analysis of which is given by the author, has a massive, cleavable structure and a bright-pink colour. Franklinite and willemite are immediately associated with it. The sp. gr. is 3·47, and the analytical results obtained were as follows:—

MnO.	CaO.	ZnO.	MgO.	FeO.	Fe_2O_3.	SiO_2.	CO_2.	Total.
45·02	11·28	2·32	1·76	0·22	0·16	0·32	38·94	100·02

B. H. B.

Kreittonite from Bodenmais. By OEBBEKE (*Jahrb. f. Min.*, 1891, i, Ref. 17).—The author found that on applying the magnet to the powder of the kreittonite of Silberberg, a green substance and a black one, magnetite, were obtained. The former gave on analysis:—

Al_2O_3.	Fe_2O_3.	FeO.	MgO.	ZnO.	Total.
48·40	7·47	14·79	2·64	27·40	100·70

B. H. B.

Occurrence of Nitrogen in Uraninite. By W. F. HILLEBRAND (*Amer. J. Sci.*, **40**, 384—394).—The author has found that nitrogen exists in uraninite in quantities up to over 2·5 per cent., and seems generally to bear a relation to the amount of uranium oxide present. This is the first discovery of nitrogen in the primitive crust of the earth. The condition in which the nitrogen exists is unknown; but it is entirely different from any hitherto observed in the mineral kingdom.

In studying the composition of uraninite in general, the author finds by analysis that this mineral from various localities varies widely in composition, and that its physical characteristics and its behaviour towards certain solvents are often as distinct as the chemical differences. The formulæ given by Comstock and by Blomstrand are inapplicable to the zirconia, thoria, and yttria uranites of North America and Norway. The author gives the results of analyses of

11 varieties of uraninite from North America and of 7 from Norway, and he proposes to continue the work in his laboratory as soon as opportunity may offer. He hopes that those possessing uraninite specimens will examine them on the lines suggested in his paper (compare Abstr., 1890, 456). B. H. B.

New Borate from Stassfurt. By L. MILCH and by O. LUEDECKE (*Zeit. Kryst. Min.*, **18**, 478—485).—This new borate is described by the two authors working independently. The analytical results they give differ so considerably that further investigation is necessary before the formula can be definitely settled. The interpretation of the crystallography of the mineral is also entirely different in the two papers.

The new borate is found, with pinnoite (Abstr., 1884, 1271), in the kainite beds of Stassfurt, in colourless, transparent, monosymmetrical crystals. The hardness of the mineral is 5, and its sp. gr. 2·127. Analysis gave the following results :—

	B_2O_3.	H_2O.	MgO.	K_2O.	Na_2O.	Cl.	Total.
I.	52·39	23·83	13·80	8·14	0·39	0·35	98·90
II.	60·53	19·85	12·23	7·39	—	—	100·00

The formulæ deduced from these two analyses are as follows :—

I. (Milch) ...... $Mg_2KB_9O_{16} + 8H_2O$.
II. (Luedecke) ... $H_2KMg_2B_{11}O_{20} + 6H_2O$.

For the new borate, Milch proposes the name of *hintzeite*, after Professor Hintze, of Breslau; whilst Luedecke proposes that of *heintzite*, after Heintz, the discover of pinnoite. B. H. B.

Apatite, Chlorite, and Mica from Belgian Localities. By C. KLEMENT (*Zeit. Kryst. Min.*, **18**, 529—530, from *Bull. Musée Roy. de Belg.*, **5**, 159).—1. *Apatite*, from the phosphorite beds of Ciply, occurring in pale, yellowish-green, transparent crystals (sp. gr. 3·226) in calcite, gave on analysis :—

P_2O_5.	F.	Cl.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.
43·49	1·31	0·57	54·49	0·42	1·46	0·33

2. *Chlorite*, from Vielsalm, in thin leaves from quartz veins, with a sp. gr. of 2·835, yielded :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	H_2O.	Total.
27·13	24·70	5·84	9·72	1·98	20·52	11·35	99·24

3. *Mica* containing chromium, from Salm-Château, in green or white layers on quartz, gave on analysis :—

SiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
45·68	34·17	0·84	2·35	0·27	3·84	4·47	2·23	4·65	98·50

B. H. B.

So-called Perofskite from Magnet Cove, Arkansas. By F. W. Mar (*Amer. J. Sci.*, **40**, 403—405).—In 1877, Knop showed that the supposed perofskite of the Kaiserstuhl contained, besides titanium, some 23 per cent. of niobium and tantalum, and he accordingly classed it as an independent species under the name of *dysanalyte*. The following analysis of a similar mineral from Magnet Cove, Arkansas, shows that it also is distinct from perofskite, and should be classed with dysanalyte :—

CaO.	MgO.	FeO.	Fe_2O_3.	$(Y,Er,Tr)_2O_3$.	$(Ce,La,Di)_2O_3$.
33·22	0·74	0·23	6·16	5·42	0·10

Nb_2O_5.	Ta_2O_5.	TiO_2.	SiO_2.	Total.	Sp. gr.
4·38	5·08	44·12	0·08	99·53	4·18

B. H. B.

Constitution of Natural Silicates. By F. W. Clarke and E. A. Schneider (*Amer. J. Sci.*, **40**, 303—312, 405—415, 452—457).—In this elaborate paper, the authors show that gaseous and aqueous hydrochloric acid differ widely in their action on magnesian silicates. In this group of minerals, the gaseous acid appears to attack only that part of the magnesium which is present as the univalent group, $\cdot Mg\cdot OH$. In favour of this view, the authors adduce a large amount of evidence. Olivine, for example, which cannot contain hydroxyl, is almost unattacked by the gas within the range of temperature studied. Serpentine, which must contain $\cdot MgOH$, is attacked proportionally to the excess of oxygen over the orthosilicate ratio. Ripidolite behaves like serpentine, and gives an analogous formula; whilst the micas, which presumably contain little or no hydroxylated magnesia, are but slightly affected. The authors are inclined to believe, on the whole, that $MgOH$ in a silicate has a lower order of stability towards gaseous hydrochloric acid than the compound $Mg(OH)_2$. B. H. B.

Eudialyte and Eucolite from Magnet Cove, Arkansas. By J. F. Williams (*Amer. J. Sci.*, **40**, 457—462).—The author gives the results of a crystallographical examination of the rare mineral eudialyte, from Magnet Cove. The crystals are transparent and crimson in colour; they may be divided, according to their form, into two classes: (1) those in which the negative rhombohedra predominate, and (2) those in which the positive ones are the larger. As a rule, the crystals are terminated above and below by hexagonal basal planes. The faces observed are $0R$, $\infty P2$, $+R$, $-\frac{1}{2}R$, $-2R$.

All those crystals which have the form and composition of eudialyte, but negative double refraction, are to be considered eucolite. Yellowish-brown crystals of this kind occurring in the Arkansas rock are to be classed under this head. From the low sp. gr. and hardness, as well as the want of complete transparency in these crystals, it is probable that they consist of decomposed eudialyte. B. H. B.

Anthophyllite from Franklin, North Carolina. By S. L. Penfield (*Amer. J. Sci.*, **40**, 394—397).—The material examined was collected at the Jenks Corundum Mine, Franklin, where it occurs in a pure and well-crystallised condition. The mineral appears never to have been fully identified from any locality in the United States hitherto. It occurs in orthorhombic crystals exhibiting only two forms, the prism and the brachypinacoid. The crystals are very transparent, and have a clove-brown colour. Their hardness is 6, and their sp. gr. 3·093. Analysis yielded the following results :—

SiO_2.	FeO.	MnO.	MgO.	CaO.	H_2O.	Al_2O_3.	Loss at 100°.	Total.
57·98	10·39	0·31	28·69	0·20	1·67	0·63	0·12	99·99*

The formula is $RSiO_3$, where R represents Mg, Fe, H_2, and traces of Mn and Ca. B. H. B.

Fowlerite Variety of Rhodonite from New Jersey. By L. V. PIRSSON (*Amer. J. Sci.*, **40**, 484—488).—The zinc-bearing rhodonite of Franklin and Stirling, in New Jersey, has been known since 1825 under the name of fowlerite. The crystalline form and physical properties have not hitherto been thoroughly investigated. The mineral occurs embedded in calcite. It is of a rose-pink colour and, in the small and perfect crystals, transparent. The axial ratios and angles measured in the crystallographical examination of this mineral agree very closely with those obtained by Flink (Abstr., 1886, 778) in his determination of the crystalline form of rhodonite from Sweden. It was also found that the two varieties differed in no appreciable degree in optical orientation. Analysis of carefully selected fowlerite gave the following results :—

SiO_2.	FeO.	ZnO.	MnO.	CaO.	MgO.	Total.
46·06	3·63	7·33	34·28	7·04	1·30	99·64

These results give the correct formula for a meta-silicate, $RSiO_3$. B. H. B.

Beryllium Minerals from Colorado. By S. L. PENFIELD (*Amer. J. Sci.*, **40**, 488—491).—During the past few years, crystals of beryl, bertrandite, and phenacite have been abundantly found associated with one another at Mount Antero, Colorado. They are implanted either on granite or on crystals of the granitic minerals, quartz, and felspar. The rare minerals bertrandite and phenacite occur in crystals of great beauty, some being of almost ideal symmetry. B. H. B.

Composition of Mica and Chlorite. By R. SCHLAEPFER (*Jahrb. f. Min.*, 1891, i, Ref. 8—9).—The author has analysed eight minerals of the mica and chlorite group with the following results :—

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* By an obvious misprint in the original, this total is stated to be 69·99.

	1.	2.	3.	4.	5.	6.	7.	8.
SiO_2...	30·11	36·18	34·06	17·09	45·05	45·35	33·24	45·38
TiO_2...	—	—	—	—	—	—	4·73	1·48
Al_2O_3..	18·31	14·34	11·75	40·40	29·94	13·95	14·90	30·16
AlF_3 ..	—	—	—	—	1·89	10·43	—	—
Fe_2O_3..	1·16	0·28	1·92	1·99	1·14	1·00	5·92	3·65
FeO ..	2·11	2·88	2·78	0·58	1·73	10·10	23·57	0·86
Cr_2O_3..	1·55	—	0·69	—	—	—	—	—
MgO ..	31·89	31·26	33·90	19·56	0·97	0·21	5·15	1·20
CaO ..	—	—	—	12·90	—	0·55	0·40	—
MnO ..	—	—	—	—	—	trace	0·95	—
K_2O...	0·37	3·09	0·39	0·43	10·23	10·88	7·77	10·49
Na_2O ..	1·99	1·99	2·45	1·86	2·13	1·55	1·45	1·83
Li_2O ..	0·31	0·42	trace	trace	—	4·06	—	—
Cl	—	—	—	0·25	—	—	—	—
H_2O ..	14·14	10·31	13·08	2·48	6·19	3·10	2·19	5·99
Total..	101·94	100·75	101·02	97·54*	99·27	101·18	100·27	101·04
Sp. gr..	2·42	2·68	2·57	2·85	2·80	1·61	3·08	2·75

1, Clinochlore from Chester, Pennsylvania; 2, from Brewster, New York; 3, pennine from Zermatt; 4, waluewite from the Ural; 5, mica from Haddam, Connecticut; 6, from Zinnwald; 7, biotite from Miask; 8, muscovite from Bamle, Norway. B. H. B.

Nepheline-syenite of the Kola Peninsula. By W. RAMSAY (*Jahrb. f. Min.*, 1891, i, Ref., 97—99).—The author gives a detailed account of the geology of the Kola peninsula, and notes the occurrence of an extensive mass of nepheline-syenite between the Lakes of Lujavr and Imaudra. In the composition of this rock, microcline, albite, nepheline, sodalite, natrolite, ægirine, arfvedsonite, ainigmite, as well as five new minerals, take part. The absence of apatite, iron ores, and titanite is noteworthy. Analyses are given of the ægirine (I), and of one of the new minerals (II):—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	51·82	0·60	21·02	8·14	1·00	3·01	1·47
II.	55·88	15·19		—	2·67	9·53	0·53

	Na_2O.	K_2O.	Ignition.	Total.	Sp. gr.
I.	11·87	0·85	0·50	100·28	3·51
II.	9·06	1·57	6·04	100·47	2·75

The latter is isotropic or very slightly birefractive, of a bright red colour, transparent, easily fusible, and soluble with difficulty in acids. B. H. B.

New Meteoric Iron from North Dakota. By O. W. HUNTINGTON (*Proc. Amer. Acad. Sci.*, **25**, 229—232).—The meteoric iron described, a specimen of special interest, was found in 1885, during the construction of a branch of the Northern Pacific Railroad, about 20 miles south-east of Jamestown, Stutsman Co., North Dakota. It weighs 4015 grams, and is of peculiar shape and appearance, in that it appears to be a thick scale blown off from the spherical surface of a large body. The iron is so malleable that it can be rolled out into thin ribbon in the cold, and it breaks like a soft, semi-solid material. The extreme malleability and peculiar fracture separate this iron from all others hitherto described. The concave side of the specimen is characterised by a vesicular structure not unlike that of certain furnace specimens. These cavities, which are distributed with some regularity in three more or less parallel zones across the shorter dimension of the surface, appear to have no connection with the pittings on the surface, and are different from anything hitherto observed in other meteoric irons. They suggest an evolution of gas from the material in process of cooling. This may have been the cause of the splitting off of the specimen from the original mass. A preliminary analysis of the iron gave the following results :—

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* The loss on ignition is 4·60, of which 2·48 is water.

Fe.	Ni.	P.	Cu.	Total.
90·24	9·75	0·05	trace	100·04

No trace of sulphur was detected. A point of interest in this iron is that it was found at the bottom of a slanting hole, rendering it probable that it belonged to a comparatively recent fall.

B. H. B.

Meteorite of Ochansk. By J. v. SIEMASCHKO (*Jahrb. f. Min.*, 1891, i, Ref. 47—48; from *Tschermak's Min. Mitth.*, **11**, 87—90).—From the examination of a considerable number of fragments of the Ochansk meteorite, the author concludes that the division of meteorites is not effected instantaneously by explosion, but by the repeated separation of fragments. In this meteorite, the brecciated structure is highly developed. The melted iron met with in the outer layer of the meteorite occurs in the form of grains or plates. One of these plates treated with acid did not exhibit Widmannstätten lines. It had the following composition :—

Fe.	Ni.	Co.	P.	S.
79·12	11·38	trace	0·74	8·44

The most noteworthy point about this meteorite is the occurrence of yellow iron sulphide in pentagonal dodecahedra, as this is the first time that iron pyrites has been observed with certainty in a meteorite.

B. H. B.

Pipe Creek Meteorite. By A. R. LEDOUX (*Jahrb. f. Min.*, 1891, i, Ref. 50; from *Trans. N. York Acad. Sci.*, **8**, 186—187).—This meteorite weighing 13½ kilos., was found in December, 1887, near Pipe Creek, 35 miles south-west of San Antonio, Texas. Analysis yielded:

Magnetic portion	30·89 per cent.
Non-magnetic portion	69·11 ,,

The magnetic portion gave:

Fe.	Ni.	Total.
90·94	9·00	99·94

and the non-magnetic portion, silicates and iron sulphide, gave—

SiO_2.	S.	CaO.	MgO.	P.	Fe_2O_3.
35·61	3·45	2·25	15·09	0·25	12·15

The analysis of a second fragment found at Waldon Ridge, Cumberland Gap, Tennessee, gave 93·86 per cent. of iron and 6·01 per cent. of nickel. B. H. B.

Meteorite from Collescipoli. By G. TROTTARELLI (*Gazzetta*, **20**, 611—615).—This meteorite, said to have fallen at Collescipoli on February 3rd, 1890, was shaped like a tortoise, and weighed about 4½ kilos.; it exploded on touching the ground, imbedding itself to the depth of half a metre. The surface was dark, dull, vitrified, covered with divergent striations, dotted over with shining particles, and pitted here and there. The interior was ash-coloured, with a granular structure, and contained numerous minute particles of metallic and nickeliferous iron, magnetic iron ore, and black nodules of ferric chromite and of pyrrhotite. When powdered, it emitted an odour resembling that of burning pyrites. Its sp. gr. in bulk is 3·71, in powder 5·313. Its composition is as follows:—

Volatile.	Na_2O.	SiO_2.	CaO.	Al_2O_3.	MgO.	Pd.
2·100	10·386	31·057	0·1169	0·9304	0·0186	0·7745

Mn.	Fe.	Cr.	Ni.	S.	O and loss.
1·006	40·983	0·5616	1·544	7·679	2·8428

and traces of phosphorus, lead, antimony, tin, potassium, lithium, sulphuric acid, and chlorine. S. B. A. A.

Organic Chemistry.

The Relative Motion of Singly-bound Carbon Atoms. By A. EILOART (*J. pr. Chem.* [2], **43**, 124—130; compare Abstr., 1888, 549; 1889, 261; 1890, 719, 899, 1083).—The author summarises this paper as follows:—(1.) There is no decisive proof that rotation occurs in the molecule of perchlorethane (compare Meyer, Abstr., 1890, 719). (2.) "The most favourable configuration" is incompatible with free rotation. (3.) Forms of a compound distinguished respectively by being capable and not being capable of rotation may exist, but we cannot distinguish such isomerides. A. G. B.

Halogen Derivatives of Amylene (Trimethylethylene). By C. HELL and M. WILDERMANN (*Ber.*, **24**, 216—223).—Chlorine acts on amylene with development of much heat, and forms a mixture of chlorinated derivatives which was found to consist of 31 parts of chloramylene, C_5H_9Cl; 44 parts of amylene dichloride, $C_5H_{10}Cl_2$; 10 parts of liquid trichloropentane, $C_5H_9Cl_3$; and a little tetrachloropentane, $C_5H_8Cl_4$. The first boils at 92—93°; the second at 130—133° (760 mm., and at 28—29° under a pressure of 12 mm.); the third at 174—180° (760 mm., and at 63—65° under a pressure of 12 mm.). These results confirm in the main those obtained by Bauer (*Zeitschr. Chem.*, 1866, 380, 667), but, unlike the latter, the authors have not obtained any solid trichloropentane, nor do they find that amylene chloride is the sole product at −17°.

Phosphorus pentachloride was found by Guthrie (this Journal, 1861, 136) to act on amylene with the formation of amylene dichloride. The authors find that chloramylenes are formed, and, under certain conditions, is trichloropentane also. If the action is allowed to take place at a low temperature, and the product at once poured on to ice, only the first two are obtained, and may be easily separated by fractional distillation; whereas if the product is allowed to become warm before pouring on to the ice, a mixture of all three compounds is obtained which it is exceedingly difficult to separate. Trichloropentane is formed both by the displacement of hydrogen in amylene dichloride and by the addition of chlorine to chloramylene, but is best prepared in a pure condition by the action of phosphorus pentachloride on the latter at 100°.

The formation of such a large proportion of chloramylene in the direct chlorination is probably due to the great heat developed in the reaction, which causes the elimination of hydrogen chloride from the amylene dichloride first formed. It follows also from the relative proportions of the products, that amylene dichloride loses hydrogen chloride more readily than it takes up another atom of chlorine by substitution, and that chlorine acts more readily on amylene than on chloramylene.

Bromine acts on amylene with the formation not only of amylene dibromide, as stated by Bauer (*loc. cit.*), but also of tribromopentane, tetrabromopentane, and isoamyl bromide; bromamylene is not formed in any appreciable quantity, probably owing to the fact that the heat of the reaction is not so great as with chlorine. *Tribromopentane* is an oily liquid which boils at 118—119° (12 mm.), is volatile in a current of steam, although scarcely so with alcohol vapour, and is scarcely attacked by boiling alcoholic potassium cyanide. *Tetrabromopentane* boils at 148—156° (12 mm.), and is also volatile in a current of steam.

By the action of bromine on amylene dibromide at 100° the above tribromo- and tetrabromopentane are obtained, together with higher brominated derivatives. A crystalline tribromopentane, melting at 207°, may be prepared, as already found by Bauer, by the addition of bromine to bromamylene, and a crystalline compound which may be identical with it is formed by the action of bromine on amylene dibromide in sunlight.

The action of bromine on amylene differs, therefore, from that of chlorine inasmuch as no bromamylene is formed, and the higher brominated products are obtained solely by substitution from amylene dibromide. H. G. C.

Cetyl Alcohol. By A. Claus and F. v. Dreden (*J. pr. Chem.* [2], **43**, 148—153).—Palmitaldehyde cannot be obtained by oxidising cetyl alcohol with chromic acid; the product of this reaction is not a single substance, as supposed by Friedau and by Dollfus (*Annalen*, **83**, 23; **131**, 287; compare Beilstein, 2nd ed., **1**, 780), but a mixture of unaltered cetyl alcohol and palmitic acid (compare Krafft, Abstr., 1880, 867).

Palmitic chloral, $C_{16}H_{20}Cl_{12}O$, is obtained by passing dry chlorine through a solution of cetyl alcohol in chloroform, first in the cold, and afterwards on the water-bath, until no more hydrogen chloride is evolved, and evaporating; it is a yellow, thick, transparent oil, becomes dark in air, has a pungent smell and sharp taste, and decomposes about 140°. The *hydrate*, $C_{16}H_{20}Cl_{12}O,H_2O$, is best obtained by shaking an ethereal solution of the chloral with water and then evaporating the ether; it is a colourless, crystalline substance. The *alcoholate* is also a solid crystalline substance insoluble in water.

When cetyl alcohol is treated with nitric acid in the cold, cetyl nitrate is obtained, but if the action is allowed to proceed too violently, pimelic, sebacic, and suberic acids are formed. The action of nitric acid on palmitic and stearic acids has been studied, and will be treated of in a future communication. A. G. B.

Inversion of Saccharose by Hydrochloric Acid. By A. Bornträger (*Chem. Centr.*, 1890, ii, 908—910; from *Zeit. Vereins Rübenzück. Ind.*, 1890, 876—905).—The author's investigations consist in a series of comparative experiments made with a view of determining which of the several methods recommended for the inversion of cane-sugar is the best. By employing the French standard weight and inverting according to Clerget's method (16·35 grams dissolved in 100 c.c. of water, of which 50 c.c. with 5 c.c. of concentrated hydrochloric acid is heated on the water-bath at 68° during 10 minutes), the observed change was 134·35 at 20°. By allowing the inversion to take place in the cold, the change = 134·69 at 20°. By employing the methods recommended by Creydt (*Deuts. Zuck. Ind.*, **13**, 807) and Wohl (*Zeits. Ver. Rub. Zuck. Ind.*, **25**, 763—771), the author arrived at results corresponding with those of Herzfeld. Since, according to the method usually employed in Germany, the solution of 13·024 grams of sugar in 50 c.c. of water and 5 c.c. of hydrochloric acid is diluted, after inversion, to 100 c.c., and then polarised, the author subjected the inverted solution prepared by Clerget's method, and which then showed a reading equal to 134·35° at 20°, also to a like dilution, when the polariscope reading corresponded with a change of 132·5° at 20°.

By employing the German method, in which 26·048 grams of sugar is dissolved in 100 c.c. of water and 50 c.c. is inverted at ordinary temperatures with 5 c.c. of concentrated hydrochloric acid, the observed change of rotation was 134·98° at 20°. By inverting according to Clerget's method the change = 134·65°. If the solution is (as is usual in Germany) diluted with water to 100 c.c. after inversion, the change = 132·8° at 20°, whereas if the solution is neutralised before diluting, the change = 134·20° at 20°.

By inverting the sugar solution, whether prepared with the French standard weight or the German, according to the method of Reichardt and Bittmann, the author found the change in rotation decidedly lower.

Among the newer methods proposed for the inversion of cane-sugar that of Herzfeld is to be recommended. 13·024 grams of the sugar is dissolved in 75 c.c. of water, 5 c.c. of 38 per cent. hydrochloric acid added, and the flask is then plunged into water of a temperature a little above 70°. The temperature of the sugar solution should rise to 68—70° within 2—3 minutes, and it is retained at this temperature in the water-bath for five minutes longer. The solution is then cooled quickly, diluted to 100 c.c., and polarised at 20°. Pure saccharose should show a change in rotation of 132·34—132·70° by this method.

The *effect of neutralising the inverted sugar solution* was found to be an increase in the polariscope reading. It was further found that the choice of base had no influence on the result, the following giving the same increase in the reading:—Sodium carbonate, sodium hydroxide, potassium hydroxide, calcium carbonate, barium hydroxide, and magnesium oxide. J. W. L.

Solubility of Sugar in Mixtures of Alcohol and Water. By C. Scheibler (*Ber.*, **24**, 434—435).—In the author's paper on this subject (*Ber.*, **5**, 343), the conclusion was drawn that solutions containing small quantities of alcohol are capable of dissolving more sugar than the water present can dissolve by itself. This conclusion is erroneous, and was brought about by an error in plotting out the curves, the fact being that all mixtures of water and alcohol dissolve less sugar than the water present is alone capable of dissolving.

H. G. C.

Gallisin, and its Method of Formation. By C. Scheibler and H. Mittelmeier (*Ber.*, **24**, 301—305; compare Fischer, this vol., p. 412).—When commercial dextrose, prepared from starch, is dissolved in water (10 parts), the dextrose completely destroyed by fermentation with yeast, and the filtered solution then evaporated to a syrup, a non-fermentable, amorphous substance, named gallisin by Cobenzl and Schmitt (Abstr., 1884, 981; 1885, 134), is obtained. This substance is wanting in all the properties of a definite chemical compound, and the formula $C_{12}H_{24}O_{10}$, assigned to it by Cobenzl, Rosenheck, and Schmitt, cannot be regarded as based on established facts; the evolution of gas, observed on heating at 100° gallisin prepared as described by Cobenzl and Schmitt, and purified with the aid of alcohol and ether, is due to the evolution of alcohol, from which the substance cannot be freed by keeping over sulphuric acid under reduced pressure.

Gallisin, purified by repeated precipitation by alcohol from its aqueous solution, is a colourless, amorphous, very hygroscopic substance; it is very readily soluble in water, the solution having a neutral reaction, and a powerful reducing action on Fehling's solution. When its aqueous solution is heated at 100° for about an hour with phenylhydrazine acetate, and then allowed to cool, a considerable quantity of a yellow osazone is deposited. This compound, purified by recrystallisation from hot water, has the composition $C_{24}H_{32}N_4O_9$, and resembles closely the osazones of the bioses in appearance; it turns brown when kept over sulphuric acid, and is only sparingly soluble in ether and acetone, but more readily in hot alcohol. It softens at about 145°, melts at 152—153°, decomposes when heated above 200°, and is rather more readily soluble in hot water than the known isomeric osazones.

These experiments show that gallisin contains a sugar of the composition $C_{12}H_{22}O_{11}$, and as gallisin yields only dextrose on hydrolysis, this sugar is probably formed by the combination of 2 mols. of dextrose in such a way that the aldehyde group of one remains unchanged (compare Scheibler and Mittelmeier, *loc. cit.*). When chemically pure dextrose (50 grams) is heated with 2½ per cent. sulphuric acid (500 c.c.) for 12 hours at 100°, the solution freed from acid and then heated with phenylhydrazine acetate, a large quantity of phenylglucosazone is deposited; if the hot solution is filtered, and then allowed to cool, a small quantity (about 0·2 gram) of an osazone, identical in properties with that described above, separates from the solution; this compound is doubtless identical with the isomaltosazone (compare Fischer, *loc. cit.*). F. S. K.

Action of Potassium Permanganate on Starch. By C. J. LINTNER (*Zeit. ang. Chem.*, 1890, 546—548).—With the object of approaching the question of the constitution of the starch molecule in a new direction, the oxidising action of potassium permanganate on starch was studied. Since both maltose and dextrose are readily oxidised by permanganate, it was anticipated that the groups which are easily hydrolysed would be the first to be destroyed by oxidation, whilst those which yield dextrin would show greater resisting power. On following the progress of the reaction by the iodine test, the same series of colours was observed as in the action of acids or of diastase. Instead of dextrin, there was produced a series of gummy acids, precipitable by lead acetate and by baryta. The operation may be performed either by adding powdered potassium permanganate to a hot 2½ per cent. starch paste, or by adding the ungelatinised starch, mixed to a milk with about 3 parts of water, to a 7½ per cent. solution of permanganate at 60—70°. Much carbonic anhydride is evolved, and manganic dioxide precipitated. With 1 part of permanganate to 2 of starch, the product gives a reddish-violet reaction with iodine, and has, when purified, a specific dextrorotatory power $[\alpha]_D = 170—182·4$; with 4 of permanganate to 3 of starch, the reaction is reddish-brown (sp. rot. power = 153·1); with 2 of permanganate to 1 of starch, the product is no longer coloured by iodine (sp. rot. power = 131·2—154·3). One of the products giving a violet colour with iodine was submitted to the action of sulphuric acid until the iodine reaction was no longer produced; it then gave a value 128·4. A similar treatment with diastase gave 130·4. This product would therefore seem to be a single substance, whilst the others are mixtures. The method of purification employed consists in filtering from the manganese precipitate, neutralising with acetic acid, concentrating to one-third the bulk, precipitating with lead acetate, washing the precipitate with hot water, and decomposing it with hydrogen sulphide. The concentrated filtrate is then poured into absolute alcohol, and the curdy precipitate is washed with absolute alcohol and ether, dried in a vacuum over sulphuric acid, and finally at 100°. The products reduce Fehling's solution to a very small extent. With phloroglucinol and hydrochloric acid, also with orcinol and hydrochloric acid, they give no characteristic colour reactions, from which fact the absence of C_5 groups may be inferred. The elementary analysis of a product which was not coloured by iodine agreed with the formula $C_{12}H_{22}O_{11},C_{12}H_{20}O_{10}$.

M. J. S.

Spermine. By W. MAJERT and A. SCHMIDT (*Ber.*, **24**, 241—243; see also this vol., p. 415).—The authors have been enabled to carry out a direct comparison of spermine and piperazine, and find that although there is great similarity between the two bases and some of their salts, they are not identical, the bismuthoiodides and the phosphates showing distinct differences. Piperazine bismuthoiodide forms microscopic rectangular plates or rods, whilst spermine bismuthoiodide crystallises in long, pointed needles, often united to feathery aggregates. Piperazine phosphate forms small, flat, four-sided tabular crystals, the angles of which are often cut off diagonally; spermine phosphate, on the other hand, crystallises in stellate aggregates of acute rounded pyramids.

Piperazine, in doses of 0·5—1·5 gram, passes through the human organism unchanged, and may be found in the urine in a very short time.

H. G. C.

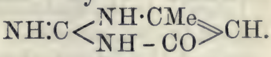
Spermine. By A. POEHL (*Ber.*, **24**, 359—360).—The author has recently prepared this base by a method resembling in principle that given by Schreiner (Abstr., 1879, 72), and finds the properties agree fully with his description. The analysis of the platinochloride, however, gave numbers which do not agree with Schreiner's empirical formula C_2H_5N, but with the formula $C_{10}H_{26}N_4$, and the analysis of the aurochloride confirmed this formula. Spermine can, therefore, be neither identical nor isomeric with piperazine.

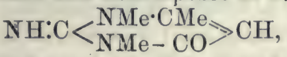
H. G. C.

Amidoximes and Azoximes. By F. TIEMANN (*Ber.*, **24**, 435—436).—The compound described by Jacoby as capronylcapramidoxime (Abstr., 1886, 785) is in reality *isocapronamide*, or *isobutylacetamide*, and melts when pure at 120° (see Hofmann, Abstr., 1884, 1114). All the substances obtained by Jacoby are derived from isocapronitrile, and should therefore have the prefix "iso-."

The substance described by Wurm as benzenylamidoximeoxalic acid, $NH_2{\cdot}CPh{:}N{\cdot}O{\cdot}CO{\cdot}COOH$ (Abstr., 1890, 259), is *benzenylamidoxime oxalate*, $NH_2{\cdot}CPh{:}NOH,H_2C_2O_4$.

H. G. C.

Methylguanicil and Trimethylguanicil. By T. Curatolo (*Gazzetta*, **20**, 585—593).—*Methylguanicil*,  $\mathrm{NH{:}C}\left<\begin{matrix}\mathrm{NH\cdot CMe}\\ \mathrm{NH-CO}\end{matrix}\right>\mathrm{CH}$. By the action of ethyl acetoacetate on guanidine carbonate in alcoholic solution, Behrend (Abstr., 1886, 338—443) obtained a substance having the composition $C_5H_7N_3O$, and analogous to methyluracil. It is best prepared by heating guanidine carbonate with a slight excess of ethyl acetoacetate at 130—150° for a few hours. The product crystallises from water in tufts of brilliant, white needles; when gently heated on platinum foil, it sublimes completely without melting; in a closed tube, it turns brown at 260—270°, and melts with complete decomposition at 292—294°. It has an alkaline reaction, dissolves moderately in boiling water, but only sparingly in cold water or boiling alcohol. It is readily soluble in warm ammonia, but on cooling the solution the base crystallises out in large prisms. It also dissolves freely in alcoholic solutions of potash or soda, forming the respective salts. The *sodium* salt, $C_5H_6NaN_3O$, forms a white, foliaceous mass mixed with shining scales. Methylguanicil is readily soluble in acids; the *hydrochloride*, $C_5H_7N_3O,HCl$, crystallises in tufts of long white needles; the *platinochloride*, $(C_5H_7N_3O)_2,H_2PtCl_6$, crystallises in large, pale-red rhombohedra insoluble in a mixture of alcohol and ether; the *formate*, $C_5H_7N_3O,CH_2O_2$, which crystallises in tufts of needles, dissolves in hot water and alcohol, and when heated at 125° splits up into formic acid and methylguanicil. The *acetate* forms amorphous nodules and decomposes at 270°.

Trimethylguanicil,  $\mathrm{NH{:}C}\left<\begin{matrix}\mathrm{NMe\cdot CMe}\\ \mathrm{NMe-CO}\end{matrix}\right>\mathrm{CH}$, is prepared by heating a mixture of methylguanicil and methyl iodide in molecular proportion with an excess of methyl alcohol for 2—3 hours at 130—140°, and decomposing the hydriodide formed with potash. It crystallises in needles, begins to decompose at 300°, and melts and partially sublimes at 320°. The *hydriodide*, $C_5H_5Me_2N_3O,HI$, crystallises in silky needles, melts at 219—220°, and dissolves readily in hot water. Determinations of the molecular weight of the two bases were made by Raoult's method, with results moderately approximating to theory.

S. B. A. A.

Olefinic Constituents of Ethereal Oils. By F. W. Semmler (*Ber.*, **24**, 201—211).—The preparation of geranaldehyde, $C_{10}H_{16}O$, has already been described (this vol., p. 30); it boils at 224—228°, under a pressure of 760 mm., and at 110—120° under a pressure of 12 mm.; the sp. gr. is 0·1972 at 15°/15°. The compound is optically inactive; the refractive index indicates the presence of two ethylene bonds, and this view is supported by the formation of a *tetrabromo*-additive compound which has not yet been obtained in crystals. Hydroxyl may be substituted for the bromine atoms, and the products thus obtained are being further investigated.

Orange oil appears to contain from 0·5 to 0·75 per cent. of oxygen; its sp. gr. is 0·8435 at 20°/20°; on treatment with hydrogen sodium sulphite, a crystalline compound is formed; on decomposing this and distilling the oily product, geranaldehyde is obtained together with a very small quantity of a lower boiling aldehyde. "Citral" is the technical term applied to an ethereal oil which is contained to the extent of 6—8 per cent. in lemon oil; this substance proves to be identical with geranaldehyde, which is also found in a number of other ethereal oils.

On heating geranaldehyde with hydrogen potassium sulphate for 20 minutes at 170°, and distilling the product in a current of steam, cymene, $C_{10}H_{14}$, is obtained, and is regarded as being formed by elimination of water from the aldehyde.

Coriander oil consists of terpenes and about 90 per cent. of another substance which is termed coriandrol, and may be readily separated by distillation under reduced pressure. *Coriandrol*, $C_{10}H_{18}O$, boils at 194—198° under a pressure of 760 mm., and at 85—90° under a pressure of 20 mm., the sp. gr. is 0·8679 at 20°/20°, and the molecular refraction 49·07; this points to the existence of two ethylene unions in the compound. It combines with 2 molecules of bromine, and on treatment with silver oxide, a hydroxyl derivative is formed.

Linaloe oil appears to be a mixture of several compounds, but no terpenes could be detected. The principal constituent, which is termed *linaloöl*, boils at about 195—190° (? 185—190°), and has a sp. gr. 0·8702 at 20°/20°; the molecular refraction is 49·33; the compound combines with 4 atoms of bromine and resembles geraniol.

A sample of "German melisse oil" gave a compound with sodium hydrogen sulphite; this was decomposed in a current of steam; the resulting product has the formula $C_{10}H_{18}O$, and boils at 204—209°; the sp. gr. is 0·8681 at 15°, and the molecular refraction 48·59. It combines directly with 2 atoms of bromine. On treating the compound $C_{10}H_{18}O$ with silver oxide, the corresponding *acid*, $C_{10}H_{18}O_2$, is obtained, which is liquid; the *silver salt* is white. On oxidation, the aldehyde yields isovaleric acid.

The above compound $C_{10}H_{18}O$ is identical with a technical product termed "citronellone" and with a compound with the same name prepared by Gladstone and Wright; it is also probably the same as the citronellic aldehyde of Dodge (compare Abstr., 1890, 231).

The author applies the term "olefinic camphenes," to compounds of the formulæ $C_{10}H_{20}O$, $C_{10}H_{18}O$, $C_{10}H_{16}O$. These, which are always open chain alcohols, aldehydes, or ketones, have a sp. gr. of 0·86 to 0·90 at 20°/20°, and a higher refractive power than the isomeric compounds with closed chains. J. B. T.

Derivatives of Acetal and Acetone. By W. AUTENRIETH (*Ber.*, **24**, 159—166).—*Chlorethylidine diethyl ether*, $CH_2Cl{\cdot}CH(OEt)_2$, is prepared by the action of sodium ethoxide on the dichlorinated derivative of the ethyl ether, and boils at 156—158°.

Thiophenyl acetal, $PhS{\cdot}CH_2{\cdot}CH(OEt)_2$, is obtained by boiling the preceding compound with sodium phenyl sulphide; it is a colourless, viscid liquid, has an aromatic odour, and boils at 273°; a cherry-red coloration is produced on heating with concentrated sulphuric acid, whilst traces of phenyl mercaptan are formed by the action of alkalis or hydrochloric acid. The yield is quantitative. All attempts to prepare thionaphthene by the action of dehydrating agents were unsuccessful; potassium permanganate also causes decomposition.

Thioethylacetal, $EtS\cdot CH_2\cdot CH(OEt)_2$, prepared from chloracetal and sodium ethyl sulphide, is a yellow liquid which boils at 168—170°, and has a powerful odour.

Phenoxylacetal, $PhO\cdot CH_2\cdot CH\cdot(OEt)_2$, is prepared by heating sodium phenoxide and chloracetal in a sealed tube for two days at 160°; on pouring into water, a heavy, colourless, oily liquid separates which boils at 254—256°. With bromine-water, a *bromo-derivative* is formed, crystallising in small, white needles, and melting at 84°.

On treating chloracetone in the cold with alcoholic solution of sodium phenyl sulphide, a compound is obtained of the formula $PhS\cdot CH_2\cdot COMe$, which the author proposes to term *thiophenylacetone*, instead of acetonylthiophenyl ether, or acetonylphenyl sulphide as heretofore. The *phenylhydrazone*, $PhS\cdot CH_2\cdot CMe{:}N_2HPh$, is deposited from alcohol in colourless crystals melting at 86—87°. No indole derivative could be obtained.

Thioethylacetone, $EtS\cdot CH_2\cdot COMe$, is prepared in a similar manner to the phenyl derivative, and is a pale-yellow, viscid liquid boiling at 170—172°. The *phenylhydrazone* is unstable and melts at 55—57°.

Phenyl bisulphide is the only substance that could be obtained by the action of ethyl chloracetoacetate on sodium phenyl sulphide. Hantzsch's results are thus confirmed. J. B. T.

Isonitrostearic Acid. By A. Claus and O. Pfeiffer (*J. pr. Chem.*, [2], **43**, 161—176).—*Isonitrostearic acid*, $C_{18}H_{35}(NO_2)O_2$, is obtained by adding, at intervals of 4—5 hours, fuming nitric acid of sp. gr. 1·48 (250—300 grams in all) to a boiling solution of stearic acid (100 grams) in glacial acetic acid (1½ litres); the heating is continued for 2 or 3 days, until a portion of the liquid does not become turbid on cooling from separation of unaltered stearic acid, and the liquid is then poured into a large quantity of cold water. The new acid is thus separated as a yellow oil which, after being washed with hot water and separated from any remaining stearic acid by slow evaporation of its alcoholic solution, solidifies to a yellowish-white, opaque, buttery mass; it dissolves in most solvents, except water and light petroleum; its melting point has not been accurately determined; it does not volatilise with steam at 110°.

Isonitrostearic acid is bibasic. The *normal potassium salt*, $K_2C_{18}H_{33}NO_4$, obtained by adding potassium hydroxide to an emulsion of the acid in water until it is neutral to phenolphthaleïn and evaporating, is a transparent, red mass, sparingly soluble in alcohol. By acting on an alcoholic solution of the acid with potassium hydrogen carbonate, a *double salt*, $K_2C_{18}H_{33}NO_4,KHCO_3$, is obtained, as well as the normal potassium salt. The *normal sodium salt* forms a yellowish-red powder, with ½ mol. H_2O; it dissolves easily in water. Attempts to obtain the ammonium salt were unsuccessful, as a deep seated reaction takes place between the acid and ammonia. The *barium*, *strontium*, and *calcium* salts were obtained by double decomposition of the alkali salts. By adding copper acetate to an aqueous solution of one of the alkali salts, a mixture of 1 mol. of the *acid copper salt*, $(C_{18}H_{34}NO_4)_2Cu$, with 2 mols. of the *normal copper salt*, $C_{18}H_{33}NO_4Cu$, is precipitated; by treating the precipitate with chloroform, the former salt is dissolved to a dark-green liquid, and remains as a dark-green, amorphous mass, when the solvent is evaporated, whilst the latter salt remains undissolved by the chloroform as a bulky, bright-green precipitate; the normal salt, which is also obtained when ether is added to a chloroform solution of the acid salt, is insoluble in all simple solvents. *Ethyl isonitrostearate* is obtained by passing dry hydrogen chloride through an alcoholic solution of the acid, and subsequently adding water; it is a heavy oil which explodes at 110°.

Experiments on the reduction of isonitrostearic acid have not as yet led to very definite results; consequently nothing is known of its structure, although its behaviour is more in accord with that of an iso- than with that of a primary nitro-compound. A. G. B.

Turkey Red Oil. By SCHEURER-KESTNER (*Compt. rend.*, **112**, 158—160).—The author has examined the sulphonated acid prepared from castor oil by the action of monohydrated sulphuric acid. It has a complex composition, but the greater part consists of a ricinoleosulphonic acid, in which the sulphonic group is united to oxygen and not to carbon (Benedikt and Ulzer). This sulphonic acid is hydrated and stable, but loses its water at 120°, and becomes insoluble. The oil also contains fatty acids formed by the decomposition or alteration of the sulphonic acid, their proportion varying with the conditions. They are polymerised acids, but the condensation does not proceed so far as stated by Juillard, the highest polymeride being diricinoleïc acid. The difference is due to the fact that Juillard added sodium chloride to the products, and this in presence of sulphuric acid liberated hydrochloric acid, which is a powerful polymerising agent. The author employed sodium sulphate as the precipitating salt.

The sulphonic acid tends to give yellowish shades, whilst the polymeric acid tends to give carmine shades with a bluish tint.

C. H. B.

Hydroxypyruvic Acid, a Product of Decomposition of Cellulose. By W. WILL (*Ber.*, **24**, 400—407).—By the action of aqueous soda on a solution of collodion wool in alcoholic ether, the mixture becomes warm, and all solid substance is taken up by the alkaline solution. When the latter is acidified, carbonic anhydride and oxides of nitrogen are evolved, and a gelatinous precipitate separates, which solidifies to a gummy, brittle mass, insoluble in water, but soluble in alcohol and alkalis. It is identical with the substance described by Eder (Abstr., 1880, 373) as cellulose dinitrate, but is in reality no longer a derivative of cellulose, as it does not yield the latter when treated with ferrous chloride, and decomposes on boiling with water, evolving hydrogen cyanide.

If the alkaline collodion solution be kept at 20° for 24—30 hours, a point is found at which acids no longer cause any precipitate. The solution reduces alkaline copper solution, which has led former investigators to assume the presence of sugars, but the results given below show this to be incorrect. If the solution is acidified with dilute sulphuric acid, warmed gently to remove oxides of nitrogen, and a mixture of phenylhydrazine hydrochloride and sodium acetate added, a compound separates at 80° which has the properties of an osazone. It crystallises from hot benzene in pale-yellow, prismatic crystals, melts at 205° with evolution of gas, when quickly heated, and has the composition $C_{15}H_{14}N_4O_2$. It would therefore appear to have the constitution

$$N_2HPh{:}CH{\cdot}C(N_2HPh){\cdot}COOH.$$

In agreement with this formula, it is found to be a strong monobasic acid; the *sodium* salt, $C_{14}H_{13}N_4{\cdot}COONa$, crystallises in pale yellow, lustrous needles, and melts at 231° with decomposition; the *potassium* salt closely resembles this and melts at 233° with decomposition; the *ammonium* salt forms very slender, pale-yellow needles, melting at 200°, and the *calcium* salt pale-yellow needles which begin to decompose at 100°, with evolution of a carbamine odour. The *ethyl* salt crystallises in long, brownish-yellow needles and melts at 149°.

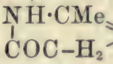
An attempt to convert the osazone into the corresponding "osone" by Fischer's method was unsuccessful, just as in the case of the osazone of glyoxal. The mother substance of the osazone was therefore prepared directly from the alkaline collodion solution; this was first acidified with sulphuric acid, the excess of the latter removed by barium nitrate, the filtrate precipitated with lead acetate, and the lead salt washed and decomposed with hydrogen sulphide. The solution on evaporation gave off carbonic anhydride, oxides of nitrogen, formic and hydrocyanic acids, and the residue, in addition to the acid yielding the above osazone, also contained oxalic acid; the latter is not, however, found in the freshly prepared solution. The mixture was evaporated to dryness, and heated until no more nitrogen remained in the residue, which was then dissolved in water, precipitated with calcium carbonate, and the filtrate precipitated a second time with lead acetate. The acid prepared from the lead salt forms a syrup which becomes solid and brittle on cooling. It has a strongly acid, astringent taste, is readily soluble in water, and is precipitated in flakes by alcohol and ether; it reduces ammoniacal copper and silver solution, and yields salts which are for the most part soluble in water. The aqueous solutions of the acid and its salts are slightly lævorotatory. The *calcium* salt, $(C_3H_3O_4)_2Ca + 8H_2O$, is a granular precipitate, which retains 4 mols. H_2O at 110°, and only loses the latter at 180°, undergoing further decomposition at the same time. The *strontium* salt, $(C_3H_3O_4)_2Sr + 4H_2O$, is similar, and the *cadmium* salt is a white compound, soluble in water.

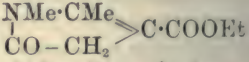
The analyses of the salts confirm the formula $C_3H_4O_4$; there are, however, two acids of this composition capable of yielding an osazone of the above constitution, namely, $CHO{\cdot}CH(OH){\cdot}COOH$ and $OH{\cdot}CH_2{\cdot}CO{\cdot}COOH$, which stand to one another in the same relation as dextrose to levulose. The acid is not oxidised by bromine-water, and is unaltered on boiling with lime and baryta-water; these properties agree best with the second of these formulæ, and the acid is therefore probably *hydroxypyruvic acid.* It shows all the reactions of an alcohol, yielding a benzoyl compound, &c. H. G. C.

Action of Ammonia and of Amines on Ethyl Acetosuccinate and its Homologues. By W. O. EMERY (*Annalen*, **260**, 137—160).—By treating ethyl acetosuccinate with ammonia, Conrad and Epstein obtained a compound which they named ethyl amidacetosuccinate, $NH_2\cdot CMe\colon C(COOEt)\cdot CH_2\cdot COOEt$ (Abstr., 1888, 253). This substance, which the author names *ethyl α-amidethylidenesuccinate*, can also be prepared by dissolving ethyl acetosuccinate in an alcoholic solution of ammonia, saturated at 0°, and keeping the solution for 24 hours at the ordinary temperature; it separates from alcohol in large, transparent, rhombic crystals, $a : b : c = 0.51504 : 1 : 0.60033$, melts at 62°, and is readily soluble in ether, alcohol, and chloroform, but rather more sparingly in carbon bisulphide, and almost insoluble in cold water. The *acetyl* derivative,

$$NHAc\cdot CMe\colon C(COOEt)\cdot CH_2\cdot COOEt$$

is produced when the ethereal salt is heated at 155—160° with acetic anhydride for several hours; it is a thick, yellow liquid, of sp. gr. 1·12873 at 20°/4°, and boils at 175—176° (about 11 mm.).

The *lactam*  $\left.\begin{array}{l}NH\cdot CMe\\ |\\ COC{-}H_2\end{array}\right> C\cdot COOEt$ is obtained when ethyl α-acetylamidethylidenesuccinate is distilled slowly under reduced pressure, or heated at 145—150° until alcohol is no longer given off. It crystallises from ether in colourless needles, melts at 133—134°, boils at 195° (about 12 mm.), and is readily soluble in alcohol, but only sparingly in ether and carbon bisulphide. It crystallises unchanged from water, combines with bromine in carbon bisulphide solution, and yields a deliquescent sodium derivative when treated with sodium ethoxide in alcoholic ethereal solution. The *acetyl* derivative, $C_{10}H_{13}NO_4$, is formed in small quantities when the lactam is heated at 155—160° with acetic anhydride; it separates from ether, in which it is sparingly soluble, as a colourless, crystalline powder, and melts at 141—142°.

A *lactam*, which has probably the constitution  $\left.\begin{array}{l}NMe\cdot CMe\\ |\\ CO-CH_2\end{array}\right> C\cdot COOEt$ is obtained when ethyl acetosuccinate is treated with anhydrous methylamine, either alone, or in alcoholic or ethereal solution, at the ordinary temperature, and the product distilled under a pressure of 11 mm. It separates from carbon bisulphide and ether, in which it is very readily soluble, in colourless crystals, melts at 42°, and boils at 160° (11 mm.); it is not converted into an acetyl-derivative by acetic anhydride at 155—160°.

A *lactam* of the composition $C_{10}H_{15}NO_3$ can be obtained from ethyl acetosuccinate and ethylamine in like manner; it crystallises in colourless needles, melts at 75—76°, boils at 165° (14 mm.), and resembles the preceding compound in its other properties.

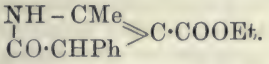
The *lactam* $C_{11}H_{17}NO_3$, prepared from ethyl acetosuccinate and propylamine in a similar manner, crystallises in colourless needles, melts at 50°, boils at 172° (14 to 15 mm.), and resembles the two preceding compounds in its behaviour with solvents.

The *lactam*, $C_{12}H_{19}NO_3$, formed by distilling the reaction-product of isobutylamine and ethyl acetosuccinate, crystallises in needles, melts at 68°, and boils at 175° (about 15 mm.). The compound $C_{13}H_{21}NO_3$, obtained from amylamine and ethyl acetosuccinate in like manner, crystallises from carbon bisulphide in plates, melts at 51—52°, and boils at 188° (16 mm.).

All the alkylated lactams described above turn yellow on exposure to the air, and are resinified by a boiling solution of barium hydroxide, but the compounds obtained by treating ethyl acetosuccinate and ethyl phenylacetosuccinate with ammonia are very stable as regards their behaviour with barium hydroxide.

A *lactam* of the composition $C_9H_{13}NO_3$ is obtained in crystals when ethyl methylacetosuccinate is mixed with alcoholic ammonia, saturated at 0°, and after keeping for 48 hours at the ordinary temperature, the solution slowly evaporated; it crystallises from ethyl acetate in small, colourless prisms melting at 127°.

A compound melting at 147—149° is formed when ethyl phenylacetosuccinate is treated with alcoholic ammonia (compare Weltner, Abstr., 1885, 793); analyses of this substance left its composition undetermined, but when it is heated at 160° for some time, it is converted into the *lactam* of ethyl α-amidoethylidenephenylsuccinate. This compound crystallises from hot ethyl acetate in colourless needles, melts at 127—128°, and is readily soluble in alcohol and ether, but rather more sparingly in carbon bisulphide and ethyl acetate; its constitution is represented by the formula



$$\left.\begin{array}{l}\mathrm{NH-CMe}\\ \mid\\ \mathrm{CO{\cdot}CHPh}\end{array}\right>\mathrm{C{\cdot}COOEt.}$$

F. S. K.

Combination of Malic Acid with Alkaline Phosphomolybdates. By D. Gernez (*Compt. rend.*, **112**, 226—229).—Measurements of the rotatory powers of solutions of malic acid with various proportions of the white alkaline phosphomolybdates of the type $3M_2O,P_2O_5,5MoO_3$ indicate in the case of the sodium and ammonium salts compounds containing respectively four equivalents of malic acid to one of the phosphomolybdate, and two equivalents of acid to three of phosphomolybdate. The potassium salt does not behave quite in the same manner, the only compound definitely indicated being one containing two equivalents of the acid and one of the phosphomolybdate. C. H. B.

Ethyl Ethoxyoxalacetate. By W. Wislicenus and M. Scheidt (*Ber.*, **24**, 432—434).—By the action of sodium ethoxide on a mixture of ethyl oxalate and ethyl ethoxyacetate, the sodium compound of ethyl ethoxyoxalacetate is formed,

$$\mathrm{COOEt{\cdot}COOEt + COOEt{\cdot}CH_2{\cdot}OEt + NaOEt =}$$
$$\mathrm{COOEt{\cdot}CNa(OEt){\cdot}CO{\cdot}COOEt + EtOH.}$$

This does not crystallise out on remaining, and is therefore at once decomposed by water, and the ethyl ethoxyoxalacetate extracted with ether. The latter is a colourless, somewhat thick oil, which boils at 155—156° (17 mm.), and is sparingly soluble in water and miscible with alcohol and ether. Its alcoholic solution is coloured deep violet by ferric chloride, and it gives a bluish-green copper salt on the addition of cupric acetate. It unites with phenylhydrazine with elimination of water, and the resulting hydrazone appears to behave in a similar manner to that of ethyl oxalacetate (Abstr., 1888, 1178).

H. G. C.

Synthesis of Alkyltricarballylic Acids and other Polycarboxylic Fatty Acids. By K. AUWERS (*Ber.*, **24**, 307—314).—Ethyl sodiomalonate combines directly with various ethereal salts of unsaturated acids, the reaction taking place very readily. Ethyl crotonate and ethyl sodiomalonate, for example, yield the compound $COOEt\cdot CHNa\cdot CHMe\cdot CH(COOEt)_2$, from which β-methylglutaric acid, $COOH\cdot CH_2\cdot CHMe\cdot CH_2\cdot COOH$, identical with the compound (m. p. 85—86°) prepared by Kommenos (Abstr., 1884, 422) is obtained on hydrolysis.

Ethereal salts of tricarballylic acid and its homologues can be easily prepared by treating ethyl fumarate with ethyl sodiomalonate and its homologues; the product is in this case a compound of the constitution $COOEt\cdot CHNa\cdot CH(COOEt)\cdot CR(COOEt)_2$, which, on hydrolysis, is converted into an acid having the constitution $COOH\cdot CH_2\cdot CH(COOH)\cdot CHR\cdot COOH$. Tricarballylic acid and its *methyl* (m. p. 180°), *ethyl* (m. p. 147—148°), *propyl* (m. p. 151—152°), and *isopropyl* derivatives were prepared in this way; these acids are all readily soluble in water and alcohol, but only sparingly in ether, and very sparingly in benzene and light petroleum. A good yield of the crude substituted tricarballylic acid is obtained in every case, but the product is very difficult to purify, probably because it is mixed with stereochemically isomeric compounds.

When tricarballylic acid is treated with acetic chloride, it loses 1 mol. H_2O, being converted into a compound melting at 131°, the constitution of which has not yet been determined.

A tetracarboxylic acid of the constitution

$$COOH\cdot CH_2\cdot CH(COOH)\cdot CH_2(COOH)\cdot CH_2\cdot COOH$$

is obtained when ethyl sodiomalonate is treated with ethyl aconitate, and the product, which has, doubtless, the constitution

$$COOEt\cdot CH_2\cdot CNa(COOEt)\cdot CH(COOEt)\cdot CH(COOEt)_2,$$

submitted to hydrolysis; the same acid is formed when the condensation product of ethyl fumarate and ethyl ethenyltricarboxylate, a substance which must have the constitution

$$COOEt\cdot CHNa\cdot CH(COOEt)\cdot C(COOEt)_2\cdot CH_2\cdot COOEt,$$

is hydrolysed. It crystallises very readily, melts at 189°, and is probably identical with the acid (m. p. 185°) obtained by Bischoff (Abstr., 1888, 1061) from ethyl butanehexacarboxylate.

F. S. K.

Action of Ethyl β-Bromopropionate on Ethyl Malonate and Ethyl Acetoacetate. By W. O. EMERY (*Ber.*, **24**, 282—286).—*Ethyl carboxyglutarate*, $COOEt\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2$, is obtained, together with a much smaller quantity of ethyl pentanetetracarboxylate when ethyl β-bromopropionate is boiled with an alcoholic solution of ethyl sodiomalonate. It is a colourless liquid of sp. gr. 1·0808 at 20°/4°, and boils at 161° (12 to 13 mm.); when hydrolysed with alcoholic potash, it yields carboxyglutaric acid as a thick syrup.

Ethyl 1:3:3:5-*pentanetetracarboxylate*,

$$COOEt\cdot CH_2\cdot C(COOEt)_2\cdot CH_2\cdot CH_2\cdot COOEt,$$

is a colourless oil of sp. gr. 1·1084 at 20°/4°; it boils at 215° (13 mm.).

1:3:5-*Pentanetricarboxylic acid*,

$$COOH\cdot CH_2\cdot CH(COOH)\cdot CH_2\cdot CH_2\cdot COOH,$$

is obtained when ethyl pentanetetracarboxylate is hydrolysed with alcoholic potash, and the syrupy acid, obtained in this way, boiled with concentrated hydrochloric acid until the evolution of carbonic anhydride is at an end; it crystallises in colourless needles and melts at 106—107°. The *silver* salt, $C_8H_9O_6Ag_3$, is colourless.

Ethyl α-acetylglutarate can be obtained by treating ethyl α-bromopropionate with ethyl sodioacetoacetate; it has a sp. gr. of 1·07115 at 20°/4°, and boils at 162° under a pressure of 11 mm. It reacts with ammonia and with amines, yielding amido-derivatives of ethyl α-ethylideneglutarate; the latter can be converted into lactams with elimination of alcohol. F. S. K.

Derivatives of Levulosecarboxylic Acid. By G. DÜLL (*Ber.*, **24**, 348—351).—The author has already described an improved method for preparing levulosecarboxylic acid (Abstr., 1890, 596).

The *ammonium* salt of levulosecarboxylic acid is formed when levulosecarboxylic acid is dissolved in the least quantity of water, saturated with ammonia, and alcohol cautiously added to the solution; it crystallises in beautiful, prismatic crystals on allowing the solution to remain over sulphuric acid.

Tetrahydroxybutanetricarboxylic acid,

$$COOH\cdot[CH\cdot OH]_3\cdot C(OH)(COOH)_2,$$

is prepared by warming levulosecarboxylic acid (10 grams) with dilute nitric acid (1 : 2, 20 grams) on the water-bath at 40° for 24 hours and evaporating the liquid at 60—70°. The syrupy mass thus obtained is converted into the calcium salt, from which the acid is liberated by shaking it up with dilute sulphuric acid (1 : 10); an equal bulk of strong alcohol is then added, the mixture allowed to remain for a time, filtered, and the alcoholic solution evaporated in a vacuum over sulphuric acid to a syrup. It crystallises in colourless tablets, becomes opaque on remaining over sulphuric acid, softens at 140°, and melts completely at 146—147°. When working with large quantities of calcium salt, the syrupy acid crystallises with difficulty to a soft, white mass, consisting of long, slender needles. The author supposes this to be a lactone; as, when a neutral solution is allowed to remain for a time, it becomes acid. The *calcium* salt, $(C_7H_7O_{10})_2Ca_3 + 6H_2O$, is purified by dissolving it in dilute hydrochloric acid, shaking with animal charcoal, and then adding sodium acetate to the warm solution until a slight precipitate remains; on cooling, the normal calcium salt separates as a crystalline mass. The *mon-acid potassium* salt, $C_7H_8O_{10}K_2$, is especially characteristic, and is obtained on evaporating an aqueous solution of the acid, two-thirds neutralised with potash, in a vacuum over sulphuric acid, in beautiful, large, prismatic crystals, and is precipitated from its aqueous solution by alcohol in microscopic, oblique prisms. The diacid potassium salt and the normal cadmium, zinc, and strontium salts were also prepared.

The *phenylhydrazide* crystallises from 50 per cent. acetic acid in long, slender, yellow needles, is insoluble in cold water, alcohol, and glacial acetic acid, dissolves in concentrated sulphuric acid with a violet colour; it begins to decompose at 200°, and then carbonises to a hard, black mass. Analysis showed that two phenylhydrazine residues were contained in the molecule.

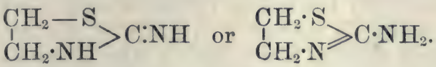
By heating the acid to a temperature slightly above its melting point, only a small quantity of carbonic anhydride was evolved. The melt contained the unaltered acid; neither saccharic, isosaccharic, metasaccharic, mucic acid, nor any other acid could be detected.

E. C. R.

Constitution of Thiocarbamide. By L. STORCH (*Monatsh.*, **11**, 452—471).—The author has endeavoured to obtain from thiocarbamide, by the action of oxidising agents, a bisulphide of the constitution $NH:C(NH_2)\cdot S\cdot S\cdot C(NH_2):NH$ (compare Maly, Abstr., 1890, 1399). The formation of such a compound would lead to the conclusion that thiocarbamide is a mercaptan, having the constitution $NH:C(SH)\cdot NH_2$, and not the symmetrical diamide $NH_2\cdot CS\cdot NH_2$. The oxidation was conducted in acid solutions with iodine, potassium permanganate, potassium chlorate, nitrous acid, and hydrogen peroxide respectively, and in every case the bisulphide was formed. The best yield was obtained when the thiocarbamide (5·5 grams) was dissolved in a mixture of water (100 c.c.) and nitric acid of sp. gr. 1·22 (110 c.c.) and the solution cooled in ice and treated with potassium permanganate (253·5 c.c. of a 0·6619 normal solution), the nitrate of the base, $C_2S_2N_4H_6(HNO_3)_2$, separated in almost insoluble prisms (yield 114—123 per cent. of the thiocarbamide employed). The new compound is gradually decomposed by water with evolution of gas at ordinary temperatures, and cannot be kept for any length of time in the dry state; its aqueous solution does not become coloured when treated with ferric chloride or copper sulphate, but gives a precipitate of silver sulphide on warming with silver nitrate; and its formation favours the view that thiocarbamide must be represented, at least in acid solution, as a mercaptan. When the oxidation is effected in presence of oxalic acid, an acid oxalate, $C_2S_2N_4H_6,2C_2H_4O_2,\frac{1}{2}H_2O$, is formed.

G. T. M.

Conversion of Alkylthiosinamines and Alkylallylsemithiocarbazides into Isomeric Bases. By C. AVENARIUS (*Ber.*, **24**, 260—271).—By the action of potassium thiocyanate on bromethylamine hydrobromide, Gabriel (Abstr., 1889, 848; 1890, 127) obtained a new base, which has one of the following constitutional formulæ:—

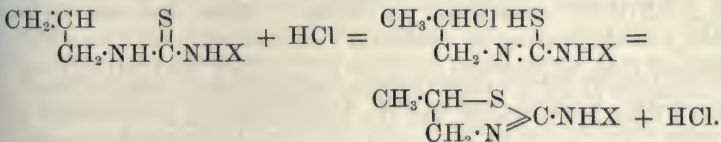


$$\left.\begin{array}{l}CH_2{-}S\\ CH_2{\cdot}NH\end{array}\right>C{:}NH \quad \text{or} \quad \left.\begin{array}{l}CH_2{\cdot}S\\ CH_2{\cdot}N\end{array}\right\geqslant C{\cdot}NH_2.$$

The corresponding derivatives containing aromatic radicles were then obtained by Prager (Abstr., 1890, 159) by an intramolecular change from aromatic allylthiocarbamides. The author has investigated the action of hydrochloric acid at 100° on the corresponding alkylallylthiocarbamides, and finds that the reaction takes place in a similar manner.

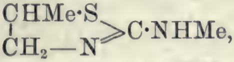
The substituted allylthiocarbamides or thiosinamines were prepared by the action of the amines on allylthiocarbimide. *Methylthiosinamine*, $NHMe{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, is a crystalline mass, melting at 46°, and sparingly soluble in water, readily in alcohol, ether, and benzene; *ethylthiosinamine*, $NHEt{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, forms colourless plates melting at 41°; *propylthiosinamine*, $NHPr^{\alpha}{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, crystallises in thin plates melting at 61°, whilst *amylthiosinamine* could only be obtained as an oil. Of the disubstituted thiosinamines, diethylthiosinamine has already been obtained by Gebhardt (Abstr., 1885, 383); *piperylthiosinamine*, $C_5H_{10}N{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, could only be obtained as an oil.

The molecular interchange takes place on heating with hydrochloric acid at 100°, and probably proceeds in the following manner:—



$$\begin{array}{l}CH_2{:}CH \qquad\quad S\\ \quad\;\; CH_2{\cdot}NH{\cdot}\overset{\|}{C}{\cdot}NHX\end{array} + HCl = \begin{array}{l}CH_3{\cdot}CHCl\;HS\\ \quad\;\; CH_2{\cdot}N{:}C{\cdot}NHX\end{array} =$$

$$\left.\begin{array}{l}CH_3{\cdot}CH{-}S\\ \quad\;\; CH_2{\cdot}N\end{array}\right\geqslant C{\cdot}NHX + HCl.$$



Methylpseudothiosinamine, $\left.\begin{array}{l}CHMe{\cdot}S\\ CH_2{-}N\end{array}\right\geqslant C{\cdot}NHMe$, is crystalline, melts at 57°, and boils without decomposition at 228°, and yields a *picrate* melting at 147°, and an oily hydrochloride. *Ethylpseudothiosinamine*, $C_4H_7NS{\cdot}NHEt$, crystallises from light petroleum in slender needles, melts at 63°, and boils at 230°. Its *hydrochloride* is also liquid, whilst the *picrate* forms slender, golden-yellow needles melting at 143°. *Propylpseudothiosinamine*, $C_4H_7NS{\cdot}NHPr^{\alpha}$, is a yellow oil which has a strongly basic odour and boils at 237°. Its *platinochloride* and *picrate* crystallise well, the latter melting at 123°. *Amylpseudothiosinamine*, $C_4H_7NS{\cdot}NH{\cdot}C_5H_{11}$, has an extremely unpleasant odour, melts at 32° and boils at 267°.

Diethylpseudothiosinamine, $C_4H_7NS{\cdot}NEt_2$, is a colourless oil which has also an unpleasant odour, and boils at 226°. Its *platinochloride* melts at 160°, and its *picrate* at 99°. *Piperylpseudothiosinamine*, $C_4H_7NS{\cdot}NC_5H_{10}$, is a yellowish oil which boils at 277°, is very sparingly soluble in water, and yields a *picrate* melting at 112°. It is an extremely stable base, and is not altered by sodium in boiling amyl alcohol solution or by phosphonium iodide at 200°. It combines with methyl iodide forming the *methiodide*, $C_4H_7NS\cdot NC_5H_{10},MeI$, a crystalline, hygroscopic substance which melts at 67°, and is extremely soluble in water. By the action of silver oxide, it yields an oil free from halogen, which is probably $C_4H_7NS\cdot NC_5H_{10},MeOH$, and has an odour resembling that of the lobster. On oxidation, piperylpseudothiosinamine is converted into β-methyltaurine, showing that the sulphur atom causes the closing of the chain.

In order to ascertain whether the alkylated pseudothiosinamines have a constitution corresponding with the first or second of the formulæ given above for the unalkylated base, ethylpseudothiosinamine was treated with ethyl iodide; the diethyl compound obtained was identical with that described above, and therefore contains both ethyl groups combined with the same nitrogen atom. The alkylated bases, as well as the aromatic derivatives obtained by Prager, must, therefore, have the constitution represented by the second formula.

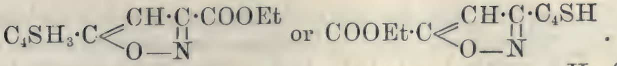
The substituted allylsemithiocarbazides undergo a similar intramolecular change when heated with hydrochloric acid. The following semithiocarbazides have been prepared:—phenylallylsemithiocarbazide, $C_3H_5\cdot NH\cdot CS\cdot N_2H_2Ph$, melting at 118° (see also Dixon, Trans., 1890, 262); *orthotolylallylsemithiocarbazide*, which forms slender needles melting at 105°; *paratolylallylsemithiocarbazide*, crystallising in small, white needles and melting at 128°; and *β-naphthylallylsemithiocarbazide*, melting at 155°.

The molecular interchange was carried out in a manner similar to that of the thiosinamines. *Phenylpropylenepseudosemithiocarbazide*, $C_4H_7NS\cdot N_2H_2Ph$, crystallises in yellowish plates, melts at 93°, and yields β-methyltaurine on oxidation; its *hydrochloride* forms stellate groups of pink crystals and melts at 202°, whilst the sparingly soluble *picrate* melts at 167°. *Orthotolylpropylenepseudosemithiocarbazide* also forms a pink *hydrochloride*, but the free base could not be obtained in crystals. The *paratolyl* compound crystallises from alcohol in slender needles melting at 133°, and the *β-naphthyl* compound forms a flocculent precipitate which, after recrystallisation from alcohol, melts at 160°.

H. G. C.

Action of Ethyl Oxalate on Acetothiënone. By A. Angeli (*Ber.*, **24**, 232—233).—Like benzophenone and pyrryl methyl ketone (Abstr., 1890, 1156, 1243), acetothiënone unites with ethyl oxalate in presence of sodium ethoxide, forming the ethyl salt of acetothiënoneoxalic acid, $C_4SH_3\cdot CO\cdot CH_2\cdot CO\cdot COOEt$, which separates from light petroleum in large, yellow crystals. It melts at 42°, gives an intense bluish-violet coloration with isatin and sulphuric acid, and is resolved by alcoholic potash into acetothiënone and oxalic acid. Its alcoholic solution gives, with cupric acetate, a *copper* compound crystallising in pale-green needles; ferric chloride gives an intense red coloration.

It yields compounds with aniline and phenylhydrazine resembling those obtained from the corresponding benzoyl and pyrroyl compounds. With hydroxylamine, it forms a substance crystallising in long, colourless needles, the constitution of which is probably represented by one of the following formulæ:—



$$C_4SH_3\cdot C{<}\begin{array}{l}CH\cdot C\cdot COOEt\\ \quad\;\, \| \\ O-N\end{array} \text{ or } COOEt\cdot C{<}\begin{array}{l}CH\cdot C\cdot C_4SH\\ \quad\;\, \| \\ O-N\end{array}.$$

H. G. C.

Biophen. By L. E. LEVI (*Chem. Centr.*, 1890, ii, 949—950; from *Technology Quarterly*, **3**, No. 2).—Just as thiophen is prepared by the action of phosphorus trisulphide on succinic acid, so also should a closed-chain compound containing two atoms of sulphur be formed by the action of phosphorus trisulphide on thiodiglycollic acid. By heating a mixture of 5 grams of thiodiglycollic acid and 10 grams of phosphorus trisulphide in 15—20 c.c. of ether in a sealed tube for two hours at 170°, a compound of the formula $S{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}S$ is formed, which the author has named *biophen*. The liquid contained in the sealed tube is washed in a separating funnel with potash, dried with calcium chloride, and the ether distilled off, after which the biophen remains as an oil. It boils at 165—170°. With sulphuric acid and isatin, it gives the indophenin reaction.

Acetobiënone is prepared by the action of acetic chloride in the presence of aluminium chloride; it is an oil which boils at 300° with decomposition. The *phenylhydrazide*, $C_4S_2H_3\cdot CMe{:}N_2HPh$, melts at 125°. *Phenyl biënyl ketone*, $C_4S_2H_3\cdot COPh$, is prepared in a corresponding manner to the acetyl derivative; it is a dark-brown oil, soluble in alcohol and ether, and boiling at 241°. *Nitrophenyl biënyl ketone*, $C_{11}H_7S_2O_3N$, is prepared by the action of nitric acid of sp. gr. 1·62 on the last-named compound, under efficient cooling; it melts at 112°.

J. W. L.

Discrimination between Allylbenzene and Propenylbenzene Derivatives by means of their Dispersive Powers. By R. NASINI (*Rend. Acad. Lincei*, **6**, ii, 299—301).—The author claims that Eykman's method of distinguishing allylbenzene from propenylbenzene derivatives (Abstr., 1890, 748) rests on Gladstone's observations (Trans., 1884, 241) and his own (*Rend. Acad. Lincei*, **1**, i; Abstr., 1885, 210 and 1097).

S. B. A. A.

Lupeol. By A. LIKIERNIK (*Ber.*, **24**, 183—186).—The term lupeol is applied to a compound obtained from the husks of *Lupinus luteus* seeds. These are extracted with ether, and the residue remaining after evaporation of the solvent is hydrolysed with alcoholic potash and dissolved in water; on treatment of the solution with ether, the lupeol dissolves, and crystallises on evaporation. It is insoluble in water, but readily dissolves in chloroform, benzene, and light petroleum; from dilute alcohol, it is deposited in long, colourless needles which melt at 204°.

Lupeol has the formula $C_{26}H_{42}O$, and therefore contains two atoms of hydrogen less than cholesterol; its rotatory power is $[\alpha]_D = +27°$; a brown coloration is produced by adding concentrated sulphuric acid to a chloroform solution, whilst the addition of acetic anhydride and two drops of concentrated sulphuric acid yields a red coloration which changes after some time to intense violet-red. The *benzoate*,

$C_{26}H_{41}{\cdot}OBz$, which may be conveniently employed to obtain pure lupeol, crystrallises from ether in lustrous, transparent prisms melting at 250°. The *acetate*, $C_{26}H_{41}{\cdot}OAc$, is deposited from dilute alcohol in feathery groups of needles melting at 230°.

On treatment with bromine dissolved in chloroform, a *bromo-derivative*, $C_{26}H_{41}BrO$, is formed, crystallising in small, colourless, nodular aggregates and melting at 150°. J. B. T.

Phenoxyethylamine and Paracresoxyethylamine. By R. SCHREIBER (*Ber.*, **24**, 189—196; compare C. Schmidt, Abstr., 1890, 373).—*Benzoylphenoxyethylamine*, $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}NHBz$, crystallises from very dilute acetic acid in slender, colourless needles, and melts at 93°. The *acetyl derivative* melts at 78°.

Bromethyl cresyl ether, $CH_2Br{\cdot}CH_2{\cdot}O{\cdot}C_6H_4Me$, is prepared by the action of sodium ethoxide on ethylene bromide and cresol; it crystallises from dilute alcohol, melts at 40°, and boils at 254—255° without decomposition.

On heating it with potassium phthalimide at 220°, *paracresoxyethylphthalimide*, $C_6H_4Me{\cdot}O{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2$, is formed, and is deposited from alcohol in pale-yellow crystals which melt at 135°; the yield is 80 per cent. of the theoretical.

Cresoxyethylphthalamic acid, $C_6H_4Me{\cdot}O{\cdot}C_2H_4{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is prepared by dissolving the preceding compound in dilute potash and precipitating with hydrochloric acid; after purification, it is obtained in silvery white crystals melting at 137°. The *silver salt* is white and crystalline. On heating the acid or imide with hydrochloric acid, and treating the product with potassium hydroxide, *paracresoxyethylamine*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, is formed; it is a colourless liquid boiling at 242—243° under a pressure of 779 mm.; on exposure to the air, a solid *carbonate* is obtained. The *hydrochloride* crystallises from alcohol in needles or plates, and melts at 240°. The *picrate*, *platinochloride*, and *aurochloride* are all crystalline; the *nitrite* appears to be stable. The *benzoyl derivative* crystallises from alcohol, benzene, or glacial acetic acid in long, slender needles, and melts at 134°.

Paracresoxyethylcarbamide, $C_6H_4Me{\cdot}O{\cdot}C_2H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$, crystallises from alcohol in needles and melts at 158°. On treating cresoxyethylphthalimide with fuming nitric acid at low temperatures, *dinitrocresoxyethylphthalimide*,

$$C_6H_2Me(NO_2)_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C_8H_4O_2,$$

is formed, crystallising from alcohol in lustrous, yellow plates, and melting at 88°. By the action of baryta-water, the nitro-groups are eliminated, and the product appears to undergo further decomposition.

Dinitroparacresol is obtained by the action of nitric acid on bromethyl cresyl ether. On heating the ether with aniline, *cresoxyethylaniline*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}NHPh$, is formed; this crystallises from alcohol in small, lustrous plates, and melts at 55°. The *hydrochloride* is crystalline.

Imidoethyl cresyl ether, $NH(CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_4Me)_2$, is prepared by the action of alcoholic ammonia on the brominated ether, and crystallises from alcohol in stellate groups of needles melting at 49—50°. The *hydrochloride* melts at 217°. On heating the ether with alcoholic potash, *ethylene tolyl ethyl ether*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$, is obtained as a colourless liquid boiling at 243—244°. With sodium methoxide, the corresponding *methyl ether*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, is formed; this resembles the preceding compound, and boils at 230°. The *phenyl ether*, $C_6H_4Me{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OPh$, prepared with sodium phenoxide, crystallises from alcohol in large, colourless plates, and melts at 99°.

Ethylene dicresyl ether, $C_2H_4(O{\cdot}C_6H_4Me)_2$, is formed by the action of potassium cyanide or dimethylaniline on bromethyl cresyl ether.

J. B. T.

Diazo-compounds of the Aromatic Series. By G. ODDO (*Gazzetta*, **20**, 631—654).—When diazobenzene chloride is gradually added to sodium ethoxide at the ordinary temperature with continual agitation, an energetic reaction takes place, accompanied by a rapid evolution of nitrogen and a strong odour of aldehyde; on steam-distilling the product, alcohol, aniline, and diphenyl pass over. If the product is diluted with water and directly distilled, aniline and ammonia are found in the distillate. The reaction is probably represented by the equation $5PhN_2Cl + 5NaOEt = PhNH_2 + NH_3 + 2C_{12}H_{10} + 5NaCl + 5Me{\cdot}COH + 4N_2$. 5 grams of aniline and 3 grams of diphenyl were obtained from 38 grams of aniline taken for diazotisation. Sodium methoxide acts like the ethoxide.

Diazobenzene chloride is not affected by methyl iodide in the cold, but on heating, much phenol and resinous products are formed, together with a very small quantity of iodobenzene. When, however, methyl iodide is slowly added to a cold mixture of the diazo-salt with the zinc-copper couple, nitrogen is evolved, and on steam-distilling the product, iodobenzene passes over; 20 grams of this compound were thus obtained from 18 grams of aniline. On treating diazobenzene chloride (0·4 mol.) at a low temperature with bromoform (0·4 mol.) and the zinc-copper couple (0·9 mol.), bromobenzene (14 grams) was obtained in like manner. An equal yield of bromobenzene may be had with one-third the above amount of bromoform if the reaction is carried out in a reflux apparatus. When diazobenzene chloride is treated with chloroform and the zinc-copper couple, a complicated reaction takes place, chlorobenzene and diphenyl being formed.

β-Bromonaphthalene is best prepared by the following modification of Gattermann's method (Abstr., 1890, 970). β-Diazonaphthalene bromide (from 14·3 grams of β-naphthylamine) is gradually added to a mixture of potassium bromide (36 grams), water 100 grams), and moist copper powder (30 grams), previously heated to 50—70°, and the whole heated in a reflux apparatus for 15 minutes and then steam-distilled. The yield is 46—48 per cent. when the naphthylamine is thoroughly diazotised. The zinc-copper couple has an action similar to that of the moist copper powder, but the yield is small.

Double Decompositions of Diazo-compounds.—If diazobenzene chloride (1 mol.) is treated with a hot solution of potassium bromide (2 mols.) in water, bromobenzene is formed, together with much resin and traces of phenol. A larger yield is obtained by slowly introducing potassium nitrite into a hot aqueous solution of aniline, hydrochloric acid, and potassium bromide. β-Bromonaphthalene can also be formed by the latter method, the yield being about 10 per cent. of the β-naphthylamine used. By adding diazobenzene chloride to a hot solution of potassium cyanide, benzonitrile is formed (1 to 1·5 grams from 9 grams of aniline); with a hot solution of potassium nitrite, nitrobenzene is obtained These reactions may be represented by the equation $PhN_2Cl + KX' = PhX' + KCl + N_2$ [$X' = Br, CN, NO_2$, &c.]. On the other hand, if potassium nitrite is added to a mixture of aniline, hydrogen bromide, and sodium chloride, no chlorobenzene, and only traces of bromobenzene are formed.

Dinitroparamidoazobenzene, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NH_2$, is prepared by adding a solution of potassium nitrite (8·5 grams) drop by drop to a hot solution of paranitraniline (13·8 grams) in hydrofluoric acid (100 c.c. of 33 to 40 per cent.), and precipitating the liquid portion of the product with water. It crystallises from alcohol in small, yellowish or brownish-red tufts, melts with partial decomposition at 210—215°, dissolves very sparingly in alcohol, ether, benzene, and chloroform, moderately in acetic acid, and very freely in solutions of alkaline hydroxides. The alkaline solutions are red, the intensity of the colour diminishing with the molecular weight of the alkali; the red coloration is more intense in alcoholic solutions. On neutralising the solution with an acid, it becomes yellow. In the preparation of this compound, a quantity of nitrophenol is formed, and, if the hydrofluoric acid used is dilute, this is the only product.

Dinitrometamidoazobenzene, prepared in like manner to the preceding compound, crystallises in minute, bright-red, rectangular prisms, melts at 193—195°, dissolves sparingly in alcohol, benzene, ether, and chloroform, but very freely in alkalis. The *acetyl* derivative melts at 145°. As bye-products in the preparation of this compound, there are obtained (*a*) a quantity of *metanitraniline hydrofluoride*, which crystallises from alcohol in light flakes and melts at 185—190°; (*b*) a small amount of ill-defined, reddish-brown crystals, melting at 183—185°, of a substance probably isomeric with the azo-compound.

The author considers that the preceding experiments, in common with Sandmeyer's and Gattermann's results, indicate that the general conditions for the double decomposition of diazo-compounds by inorganic salts, with elimination of the diazo-group, are that the inorganic and the diazo salt should be of the same character, and that the radicle combined with the diazo-group should be more electronegative than that contained in the inorganic salt. In concluding, the author discusses some of his results from a thermochemical point of view.
S. B. A. A.

Stability of Diazo-compounds in Aqueous Solution. By R. Hirsch (*Ber.*, **24**, 324—326).—A solution of diazo-orthotoluene in phenol decomposes much more easily than a similar solution of diazoparatoluene. Aqueous solutions of the diazo-compounds behave in a similar manner. The author determines quantitatively the relative stability of diazo-compounds in the following way.

Aniline (9·3 grams), orthotoluidine and paratoluidine (10·7 grams), metaxylidine (12·1 grams), and sulphanilic acid (17·3 grams) are severally dissolved in water (700 c.c.) and hydrochloric acid (30 c.c.), and then diazotised with nitrite (7·2 grams), dissolved in water, and the solution made up to 1 litre. A solution of sodium naphtholsulphonate (Schaeffer's salt) is made to correspond with the diazo-solution. The diazo-solutions are then allowed to remain at the ordinary temperature, and the amount of decomposition estimated from time to time as follows:—25 c.c. of the naphthol solution is mixed with a few drops of ammonia and some salt, and the diazo-solution run in from a burette as long as any dye is formed. The results obtained show that the introduction of a methyl group in the para-position into diazobenzene greatly increases the stability, whilst a methyl group in the ortho-position lessens the stability. Metaxylidine stands between orthotoluidine and paratoluidine as regards the stability of its diazo-compound, whilst diazoparaxylidine is more easily decomposed than diazo-orthotoluene. Experiments on the stability of diazobenzene solutions under different conditions showed that the best way to prevent decomposition was to keep the solution cold; the addition of acid prevents decomposition to some extent; sodium acetate and alkalis have no appreciable effect.

E. C. R.

Dry Decomposition of Diazoamido-compounds. By F. HEUSLER (*Annalen*, **260**, 227—250).—When diazoamidobenzene (1 mol.) is mixed with liquid paraffin (8—10 parts) and then very gradually heated to 150°, slow decomposition ensues with evolution of nitrogen (1 mol.); the products are benzene, aniline, diphenyl, paramidodiphenyl, and orthamidodiphenyl. The *acetyl* derivative of paramidodiphenyl melts at 171°, that of the ortho-compound at 119°.

The diazoamido-derivatives of paratoluidine and parachloraniline seem to yield, under the same conditions, decomposition products analogous to those obtained from diazoamidobenzene, but the formation of diphenyl-derivatives could not be determined with certainty.

When benzenediazobenzylanilide is heated with paraffin in the manner described above, it is decomposed into benzene, benzylanilide, small quantities of diphenyl, and benzylideneaniline; the formation of the last-named compound is shown by the fact that when the mixture of decomposition products is treated with hydrochloric acid, benzaldehyde and aniline are obtained.

In studying the decomposition of benzenediazopiperidide, a considerable quantity (250—300 grams) of the dry compound is gradually heated in a large flask, and the decomposition products passed through a Linnemann's dephlegmator, to which is attached a condenser; the temperature of dissociation is about 225—230°, but in order to complete the decomposition, the temperature must finally be raised to about 250°. The residue consists of diphenyl (10 per cent. of the theoretical quantity) and tarry matters; the distillate contains benzene (52 per cent. of the theoretical quantity), piperidine, small quantities of aniline, and a basic substance which the author names isopiperideïne.

Isopiperideïne is a thick, sticky liquid, with a strong, narcotic odour, and miscible with water in all proportions; it seems to have the composition C_5H_9N, but there are several facts which tend to show that it is a mixture. On distillation under the ordinary pressure, it passes over between 260° and 290°, and even on repeated fractionation, a liquid of constant boiling point cannot be obtained. All the salts, except the platinochloride, which crystallises in ruby-red needles, are very hygroscopic, and cannot be obtained in a pure condition for analysis. Isopiperideïne reacts with acetic anhydride and with benzoic chloride, yielding oily products, and it combines very energetically with methyl iodide with formation of a very hygroscopic additive compound; benzyl chloride and phenyl cyanate combine with the base very readily, the products being oils; diazobenzene chloride converts it into a yellow, solid compound which very readily resinifies. When isopiperideïne is treated with carbon bisulphide in ethereal solution, a yellow substance, which seems to have the composition $2C_{10}H_{18}N_2,CS_2$, is precipitated; this compound is decomposed when warmed, either alone or with dilute sulphuric acid, with evolution of hydrogen sulphide. Isopiperideïne has powerful reducing properties, gives the carbylamine reaction, and its hydrochloride is partially decomposed by sodium nitrite in the cold; with aqueous solutions of formaldehyde and acetaldehyde it gives colourless, seemingly amorphous precipitates which are soluble in acids, but are reprecipitated by alkalis.

Benzenediazodimethylamide, $Ph\cdot N_2\cdot NMe_2$, can be obtained in a pure condition by treating an alkaline solution of dimethylamine with diazobenzene chloride, extracting the precipitated oil with ether, and fractionating the dried product under reduced pressure. It is a yellowish, highly refractive liquid, boils at 113—114° (12 mm.), and has a sp. gr. of 1·032 at 18°; when dropped on to sand heated to 253°, it is decomposed into benzene, diphenyl, dimethylamine, and small quantities of a liquid base which was not investigated.

F. S. K.

Action of Phosphorus Pentachloride on Oxyazo-derivatives.

By R. Paganini (*Ber.*, **24**, 365—369; compare this vol., p. 301).—*Paratoluene-azochlorobenzene*, $C_6H_4Me\cdot N_2\cdot C_6H_4Cl$, is prepared by the action of phosphorus pentachloride on paratoluene-azophenol, and crystallises from alcohol in long, orange-yellow needles melting at 149—150°; it is very sparingly soluble in concentrated hydrochloric acid, insoluble in alkalis, and on sublimation forms large, yellow plates.

Paratoluene-azophenyl phosphate, $PO(O\cdot C_{13}H_{11}N_2)_3$, is formed together with the preceding compound; it is insoluble in alcohol, but crystallises from acetone in long, lustrous needles, melts at 140°, and is readily hydrolysed by alcoholic potash.

Orthotoluene-azophenol, $C_6H_4Me\cdot N_2\cdot C_6H_4\cdot OH$, is obtained by treating orthotoluidine hydrochloride with nitrous acid, and adding an alkaline solution of phenol; the solution is cooled, and the compound precipitated with carbonic anhydride; after purification, it crystallises from benzene in thick, orange-yellow needles, melts at 101°, and is soluble in dilute ammonia.

Phenoldisazorthotoluene, $OH\cdot C_6H_3(\cdot N_2\cdot C_6H_4Me)_2$, is separated from the previous compound by treatment with dilute ammonia, in which it is very sparingly soluble; it crystallises from alcohol in thin, slender, brownish-red needles, and melts at 116—117° with decomposition.

Orthotoluene-azochlorobenzene, $C_6H_4Me\cdot N_2\cdot C_6H_4Cl$, is prepared in a similar manner to the para-derivative, and crystallises from alcohol in small, yellow needles melting at 143—144°.

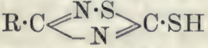
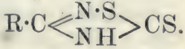
Orthotoluene-azophenyl phosphate, $PO(O\cdot C_{13}H_{11}N_2)_3$, is sparingly soluble in cold alcohol, and crystallises from acetone in long, orange-needles melting at 116°.

Metatoluene-azophenol is prepared in a similar manner to the ortho-compound, and crystallises from alcohol in yellow cubes melting at 141°. On treatment with phosphorus pentachloride, a compound is obtained in small quantity, which crystallises from alcohol in yellow needles melting at 65°, and is probably *metatoluene-azochlorobenzene*, $C_6H_4Me\cdot N_2\cdot C_6H_4Cl$. J. B. T.

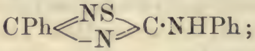
Sulphur Derivatives of Amidoximes. By F. Tiemann (*Ber.*, **24**, 369—377).—Compounds free from sulphur are obtained by the action of hydroxylamine on thiocarbimides.

Carbon bisulphide reacts with amidoximes according to the equation

$$2NH_2\cdot CR{:}NOH + 3CS_2 = NSH{:}CR\cdot NH\cdot CSSH, NH_2\cdot CR{:}NSH + 2COS;$$

these compounds, which may be termed *amidosulphimes of dithiocarbamidosulphinic acids*, are very unstable, and on treatment with hydrochloric acid yield amidine hydrochlorides, carbonic anhydride, hydrogen sulphide, and sulphur; on heating the above compounds alone, however, stable derivatives are obtained containing the group $RC_2N_2HS_2$; the same substances, together with amidine thiosulphates, are also formed by heating the sulphinic acid derivatives in air. The constitution of the complex $RC_2N_2HS_2$ is probably represented by one or other of the formulæ  $R\cdot C{<}\begin{smallmatrix}N\cdot S\\ N\end{smallmatrix}{\geqslant}C\cdot SH$;  $R\cdot C{<}\begin{smallmatrix}N\cdot S\\ NH\end{smallmatrix}{>}CS$. On heating with hydrochloric acid at 150°, decomposition takes place according to the equation $RC_2N_2HS_2 + 4H_2O + 2HCl = R\cdot COOH + CO_2 + 2NH_4Cl + H_2S + S$; on oxidation, 2 mols. combine together with elimination of 1 mol. of hydrogen, and by the action of reducing agents the original compound is regenerated; this behaviour appears to be most readily explained by the first formula, and it is proposed to term the substances *azosulphimecarbohydrosulphides*, in order to show the analogy with the azoximes.

On heating benzenylphenylthiouramidoxime in chloroform solution with phenylthiocarbimide, water is eliminated, and a compound is formed which is probably *benzenylazosulphimecarbanilide*,



$$\mathrm{CPh}{<}^{\mathrm{NS}}_{-\mathrm{N}}{>}\mathrm{C{\cdot}NHPh};$$

it does not yield aniline on treatment with hydrochloric acid, and is completely unacted on by carbon bisulphide.

Benzenylparatolylthiouramidoxime yields a corresponding product when heated a little above its boiling point. J. B. T.

Action of Hydroxylamine, Ethoxylamine, and Benzyloxylamine on Thiocarbimides. By L. VOLTMER (*Ber.*, **24**, 378—385; compare preceding abstract).—*Phenylhydroxylthiocarbamide*, NHPh·CS·NH·OH, is prepared by mixing together phenylthiocarbimide and hydroxylamine in molecular proportions; after about 20 minutes, the mixture is well shaken, and allowed to remain for 20 hours at a temperature below 0°; the crystals which form are separated and washed with chloroform. The compound melts at 106° with evolution of gas, and gives a dark-violet coloration with ferric chloride; it cannot be recrystallised, but dissolves readily in potash, and is precipitated unchanged by acids. No salts could be isolated. When boiled with alcohol, or when fused, sulphur is eliminated and phenylcyanamide is formed; the same change takes place slowly at ordinary temperatures.

Phenylethoxythiocarbamide, NHPh·CS·NH·OEt, is obtained from phenylthiocarbimide and ethoxylamine in a similar manner to the preceding compound, and crystallises from alcohol in colourless, strongly refractive, prismatic plates melting at 103°. The compound is comparatively stable, it gives no coloration with ferric chloride, and when boiled in alcoholic solution, phenylcyanamide, alcohol, and sulphur are formed. *Phenylmethoxythiocarbamide*, NHPh·CS·NH·OMe, prepared from phenylthiocarbimide and methoxylamine, crystallises from alcohol in lustrous needles, and melts at 115°; the yield is very small.

Phenylbenzyloxythiocarbamide, NHPh·CS·NH·O·CH_2Ph, crystallises from alcohol in prisms melting at 115°.

Orthotolylhydroxythiocarbamide, C_6H_4Me·NH·CS·NH·OH, is prepared from orthotolylthiocarbimide and hydroxylamine; it is deposited from chloroform in long, slender needles, melts at 92°, and yields an intense violet coloration with ferric chloride.

Orthotolylcyanamide, C_6H_4Me·NH·CN, is formed by the decomposition of the preceding compound either at the ordinary temperature or on boiling in solution, but is best prepared by the action of hydroxylamine on orthotolylthiocarbimide at higher temperatures; it crystallises from ether in rhombic plates, melts at 77°, and is readily soluble in alcohol, chloroform, and alkalis, but rather more sparingly in acids. The *silver salt* decomposes on exposure to light.

Orthotolylbenzyloxythiocarbamide, C_6H_4Me·NH·CS·NH·O·CH_2Ph, is deposited from alcohol in crystals, melts at 125°, and closely resembles the corresponding phenyl derivative.

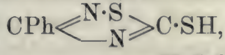
α-Naphthylhydroxythiocarbamide, $C_{10}H_7$·NH·CS·NH·OH, crystallises from alcohol in lustrous plates, melts at 116°, and gives a dark bluish-green coloration with ferric chloride. *α-Naphthylcyanamide*, $C_{10}H_7\cdot NH\cdot CN$, is obtained by heating an alkaline solution of the preceding compound, and crystallises from alcohol in aggregates of slender needles melting at 135°; the addition of a little potash to an alcoholic solution causes a blue fluorescence. The *silver salt* is white. On heating the amide with hydrochloric acid, a compound is formed which is indifferent towards alkalis and dilute acids, and crystallises in slender needles melting at 209—210°. *α-Naphthylbenzyloxythiocarbamide*, $C_{10}H_7\cdot NH\cdot CS\cdot NH\cdot O\cdot CH_2Ph$, melts at 132—133°. No additive product could be obtained from allylthiocarbimide and hydroxylamine.

Phenylbenzyloxycarbamide, $NHPh\cdot CO\cdot NH\cdot O\cdot CH_2Ph$, is prepared by the action of benzylhydroxylamine on phenyl isocyanate in molecular proportion; on the addition of light petroleum to its solution in benzene, it crystallises in long needles melting at 106°. The compound is very stable, and requires heating for a considerable time with hydrochloric acid before decomposition takes place; it is readily soluble in alcohol, ether, and chloroform, but more sparingly in hot water. J. B. T.

Action of Carbon Bisulphide on Benzenylamidoxime and Parahomobenzenylamidoxime. By G. Crayen (*Ber.*, **24**, 385—393; compare Schubart, Abstr., 1890, 49).—*Benzenylamidosulphime benzenylsulphimedithiocarbamate*,

$$NSH\!:\!CPh\cdot NH\cdot CSSH,NH_2\cdot CPh\!:\!NSH,$$

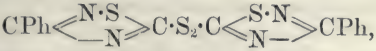
is prepared by heating carbon bisulphide with dilute alcoholic solution of benzenylamidoxime for 3—4 hours in a reflux apparatus. After remaining for 2—5 days at the ordinary temperature, the crystals which form are separated, and purified by washing with benzene, light petroleum, and ether; they melt at 134—136° with decomposition, and cannot be recrystallised.

By treatment with hydrochloric acid or soda, benzenylamidine is formed; on heating at 100° in air, *benzenylazosulphimecarbohydrosulphide*,  $CPh{<}\substack{N\cdot S\\ N}{>}C\cdot SH$, and *benzenylamidine thiosulphate*,

$$H_2S_2O_3,2NH_2\cdot CPh\!:\!NH,$$

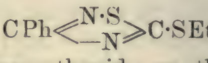
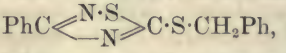
are obtained; the former is soluble in alcohol, and crystallises in needles melting at 162°. The compound, which has previously been prepared by Schubart (*loc. cit.*), yields salts with metals, the *mercury derivative* being the most characteristic. The above thiosulphate is deposited from water, on the addition of acetone, in small, lustrous plates melting at 222°.

Benzenylazosulphimecarbobisulphide,



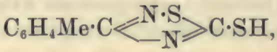
$$CPh{<}\substack{N\cdot S\\ N}{>}C\cdot S_2\cdot C{<}\substack{S\cdot N\\ N}{>}CPh,$$

is prepared by the oxidation of the hydrosulphide with nitric acid, chromic anhydride, or potassium permanganate; it is sparingly soluble in alcohol or ether, and crystallises in concentric needles melting at 120°. The hydrosulphide is regenerated on treatment with sodium amalgam and alcohol.

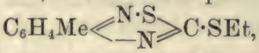
Benzenylazosulphimecarbothioethyl ether,  $\mathrm{CPh}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot SEt}$, obtained by the action of ethyl iodide and sodium ethoxide on the hydrosulphide, crystallises from dilute alcohol, and melts at 49°. The corresponding *benzyl ether*,  $\mathrm{PhC}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot S\cdot CH_2Ph}$, melts at 79°.

Parahomobenzenylamidosulphime parahomobenzenylsulphimedithiocarbamate, $\mathrm{C_6H_4Me\cdot C(NSH)\cdot NH\cdot CSSH,NH_2\cdot C(C_6H_4Me){:}NSH}$, is prepared in a similar manner to the benzenyl derivative; it is very unstable, cannot be recrystallised, and is immediately decomposed when heated. By the action of hydrochloric acid, *parahomobenzenylamidine hydrochloride*, $\mathrm{C_6H_4Me\cdot C(NH)\cdot NH_2,HCl}$, is formed; this crystallises in colourless prisms melting at 212°. The *platinochloride* melts at 225°.

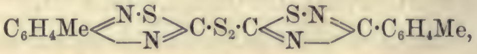
Parahomobenzenylazosulphimecarbohydrosulphide



$$\mathrm{C_6H_4Me\cdot C}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot SH},$$

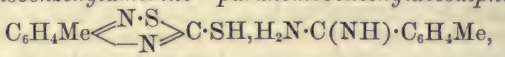
is obtained from the mother liquors of the above dithiocarbamate by treatment with hydrochloric acid, and has been previously prepared by Schubart. The *ethyl ether*,  $\mathrm{C_6H_4Me}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot SEt}$, crystallises from ether in large, transparent plates melting at 37°.

Parahomobenzylazosulphimecarbobisulphide,



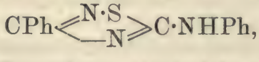
$$\mathrm{C_6H_4Me}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot S_2\cdot C}\left\langle\begin{matrix}\mathrm{S\cdot N}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot C_6H_4Me},$$

is formed by the oxidation of the hydrosulphide with nitric acid, and crystallises from benzene, on the addition of absolute alcohol, in slender, white needles melting at 169°.

Parahomobenzenylamidine parahomobenzenylazosulphimecarbohydrosulphide,  $\mathrm{C_6H_4Me}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot SH,H_2N\cdot C(NH)\cdot C_6H_4Me}$, is deposited from the mother liquors of the amidosulphimesulphimate in colourless, well-developed crystals which melt at 172°. On treatment with hydrochloric acid, the compound is decomposed into the amidine hydrochloride and the hydrosulphide, and it may be directly prepared from these components.

J. B. T.

Condensation Products from Thiouramidoximes. By H. Koch (*Ber.*, **24**, 394—399).—Benzenylphenylthiouramidoxime, $\mathrm{NOH{:}CPh\cdot NH\cdot CS\cdot NHPh}$, is colourless, and melts at 172°, instead of 163°, as stated by Krüger. When heated in chloroform solution with two molecular proportions of phenylthiocarbimide for 10 hours in a reflux apparatus, *benzenylazosulphimecarbanilide*,

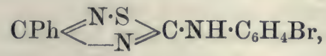


$$\mathrm{CPh}\left\langle\begin{matrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{matrix}\right\rangle\mathrm{C\cdot NHPh},$$

is formed; this crystallises from alcohol in small, white plates, and melts at 174°. On heating it with hydrochloric acid in a sealed tube at

150—160°, it yields sulphur, hydrogen sulphide, aniline, ammonia, and benzoic acid.

Benzenylazosulphimecarboparabromanilide,



$$\mathrm{CPh}<\begin{smallmatrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{smallmatrix}>\mathrm{C\cdot NH\cdot C_6H_4Br},$$

is prepared by treating the anilide with bromine in glacial acetic acid solution; after precipitation with water, the product crystallises from alcohol in small, white plates; when heated, it decomposes without melting. The constitution of the compound is shown by the formation of parabromacetanilide on hydrolysis and subsequent treatment with glacial acetic acid.

Benzenylazosulphimecarbonitrosoanilide, $\mathrm{CPh}<\begin{smallmatrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{smallmatrix}>\mathrm{C\cdot NPh\cdot NO}$, is prepared by treating the azosulphime, in glacial acetic acid solution, with sodium nitrite; it crystallises in yellow needles, melts at 190° with decomposition, and gives the nitroso-reaction with phenol and sulphuric acid. The *acetanilide,* $\mathrm{CPh}<\begin{smallmatrix}\mathrm{N\cdot S}\\ \mathrm{N}\end{smallmatrix}>\mathrm{C\cdot NAcPh}$, is formed by heating the anilide with acetic anhydride, and melts at 196°.

Benzenylparatolylthiouramidoxime, $\mathrm{NOH\colon CPh\cdot NH\cdot CS\cdot NH\cdot C_6H_4Me}$, prepared from benzylamidoxime and paratoluylthiocarbimide, is purified by solution in benzene, and precipitation with light petroleum; it melts at 67°, and readily decomposes.

Benzenylazoximecarboparatoluidide, $\mathrm{CPh}<\begin{smallmatrix}\mathrm{N\cdot O}\\ \mathrm{N}\end{smallmatrix}>\mathrm{C\cdot NH\cdot C_6H_4Me}$, is prepared by heating benzenylamidoxime with paratoluylthiocarbimide, and crystallises from alcohol in small plates melting at 135°.

Benzenylallylthiouramidoxime, $\mathrm{NOH\colon CPh\cdot NH\cdot CS\cdot NH\cdot C_3H_5}$, is obtained in a similar manner to the preceding compound; on the addition of light petroleum to its solution in benzene, it crystallises out in slender, silky needles melting at 71°. All attempts to obtain condensation compounds from it were unsuccessful. J. B. T.

Reduction of Aromatic Amides. By A. HUTCHINSON (*Ber.*, **24**, 173—178; compare E. Fletcher, Abstr., 1890, 597).—Aromatic amides containing the carboxyl group linked to the benzene nucleus are readily reduced to the corresponding alcohol by the action of sodium amalgam in acid solution, a certain quantity of resinous matter being also formed. The amides examined were those of orthotoluic acid, salicylic acid, parahydroxybenzoic acid, and paramethoxybenzoic acid.

With the carboxyl group in the side chain, a different result is obtained; thus phenylacetamide is unaltered, and cinnamide yields phenylpropionamide.

The behaviour of phenylacetamide, phenylpropionamide, and salicylamide in alkaline solution is the same as in acid solution.

Paramethoxybenzamide in alkaline solution, in addition to the products just mentioned, yields considerable quantities of anisoïl.

Benzamide yields benzyl alcohol, resinous matter, and about 7 per cent. of *dihydrobenzamide,* $\mathrm{C_6H_7\cdot CONH_2}$, crystallising from water or alcohol in silvery, lustrous plates, and melting at 152—153°. This compound is unaffected by nascent hydrogen. When treated with alkalis it is hydrolysed; the *dihydrobenzoic acid* thus formed melts below 100°, and is readily soluble in water.

Orthotoluamide behaves exactly like benzamide; *orthodihydrotoluamide*, $C_6H_6Me{\cdot}CONH_2$, crystallises from water, and melts at 155—156°. The corresponding *acid* melts at 68°, and is volatile with steam. J. B. T.

Nitro- and Amido-derivatives of Phenylacetamide. By A. Purgotti (*Gazzetta*, **20**, 593—600).—The author has previously described (this vol., p. 59) the formation of phenylacetamide by the action of concentrated sulphuric acid on benzonitrile; the following derivatives have now been examined.

Paranitrophenylacetamide, $NO_2{\cdot}C_6H_4{:}CH_2{\cdot}CONH_2$, is prepared by introducing phenylacetamide in small quantities at a time into a well-cooled mixture of an equal weight of nitric acid and twice its weight of sulphuric acid, allowing it to remain for a few hours, and pouring it into an excess of water. After purification, it crystallises from boiling alcohol in colourless, acicular prisms, melts at 197—198°, dissolves freely in hot water and acetic acid, but only very sparingly in ether, benzene, and cold water. On boiling with dilute sulphuric acid, it is converted into paranitrophenylacetic acid melting at 150—151°.

Metanitrophenylacetamide is prepared by evaporating at the ordinary temperature the mother liquors obtained in the preparation of the preceding compound. It crystallises in microscopic, hexagonal pyramids, melts at 109—110°, and dissolves freely in cold water and in benzene. On boiling it with a solution of sodium hydroxide, ammonia is evolved, and sodium metanitrophenylacetate remains.

Paramidophenylacetamide, prepared by reducing the corresponding nitro-derivative with ammonium sulphide, crystallises in glistening scales, melts at 153—154°, dissolves readily in cold alcohol and warm water, but only sparingly in benzene.

Paracetamidophenylacetamide, $NHAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}CONH_2$, prepared by heating a mixture of the preceding compound with acetamide in molecular proportion at 160—170°, forms a white, amorphous powder, melts at 235°, and dissolves sparingly in boiling water. On boiling with dilute sulphuric acid, it is converted into the sulphate of paramidophenylacetic acid. S. B. A. A.

Derivatives of Cinnamaldehyde. By A. Naar (*Ber.*, **24**, 244—252).—Chlorine acts on cinnamaldehyde in chloroform solution in a manner similar to bromine (Abstr., 1884, 1343), forming the additive compound $CHPhCl{\cdot}CHCl{\cdot}COH$, which, however, loses hydrogen chloride very readily, forming *α-chlorocinnamaldehyde*, $CHPh{:}CCl{\cdot}COH$. It is best prepared by boiling an acetic acid solution of the dichloride with potassium acetate, and crystallises from a mixture of ether and light petroleum in large, lustrous, rhombic crystals melting at 34—36°. Its *oxime*, $CHPh{:}CCl{\cdot}CH{:}NOH$, crystallises in long plates melting at 157—159°; its *hydrazone*,

$CHPh{:}CCl{\cdot}CH{:}N_2HPh$, in narrow, yellow plates melting at 160°, and becoming brown in the air, and the compound with dimethylparadiamidobenzene, $CHPh{:}CCl{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NMe_2$, in orange-yellow needles, which are decomposed by heating with acids.

α-Bromocinnamaldoxime, $CHPh{:}CBr{\cdot}CH{:}N{\cdot}OH$, crystallises in nacreous plates melting at 135—136°, and the dimethylparadiamidobenzene compound in yellow scales melting at 253—255°.

Both α-chlorocinnamaldehyde and α-bromocinnamaldehyde are readily acted on by nitric acid, with simultaneous formation of ortho- and para-derivatives. *Paranitrochlorocinnamaldehyde*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}CCl{\cdot}COH,$$

crystallises in yellow needles melting at 145°, which may be separated from the ortho-compound by their insolubility in ether. The *oxime* crystallises from alcohol in yellowish needles melting at 213—215°; the *hydrazone* in cinnabar-red plates melting at 179°; and the dimethylparadiamidobenzene compound in dark-brown needles melting at 185°. *Orthonitrochlorocinnamaldehyde* forms yellowish needles melting at 112—113°; the *oxime* crystallises in a similar manner, and melts at 191°; the *hydrazone* forms yellowish plates, which become brown in the air, and melts at 140—141°, whilst the dimethylparadiamidobenzene compound forms reddish-brown prisms melting at 128—130°. The corresponding ortho- and para-nitrobromocinnamaldehydes have been already described (*loc. cit.*). Their *oximes* form yellow needles melting at 161—162° and 205—207° respectively, and the dimethylparadiamidobenzene compounds crystallise in lustrous, bronze-coloured needles, both melting at 172—173°.

By the oxidation of α-chlorocinnamaldehyde, the corresponding α-chlorocinnamic acid, $CHPh{:}CCl{\cdot}COOH$, melting at 138—139°, is formed; it has already been frequently prepared. It gives a characteristic *barium* salt $(C_9H_6ClO_2)_2Ba + H_2O$, which crystallises from hot water in lustrous plates. Paranitrochlorocinnamaldehyde yields the corresponding acid with chromic acid, but is converted into paranitrobenzoic acid on further oxidation. *Orthonitrochlorocinnamic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}CCl{\cdot}COOH$, is obtained in a similar manner, and crystallises from water in lustrous needles melting at 201—202°; it is completely destroyed by further oxidation. The brominated derivatives behave in a similar manner; *orthonitro-α-bromocinnamic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}CBr{\cdot}COOH$, forms slender, colourless needles, and melts with decomposition at 211—212°.

Metanitrocinnamaldehyde is also acted on by chlorine forming an additive product, which readily loses hydrogen chloride yielding *metanitro-α-chlorocinnamaldehyde*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}CCl{\cdot}COH$. This crystallises from alcohol in pale-yellow plates melting at 112°; its *oxime* forms yellowish needles which melt at 185—186°, its *hydrazone* pale-yellow scales melting at 154—156°, and the dimethylparadiamidobenzene derivative, obtuse, brown needles melting at 225—227°. The corresponding *metanitro-α-bromocinnamaldehyde* and its *hydrazone* have been prepared by Kinkelin (Abstr., 1885, 791); the *oxime* crystallises in pale-yellow needles melting at 199—200°, and the dimethylparadiamidobenzene compound in reddish-brown prisms

melting at 145—147°. *Metanitrochlorocinnamic acid* and *metanitrobromocinnamic acid* are obtained by the oxidation of the aldehydes, and crystallise in colourless, matted needles melting at 205—207° and 211—213° respectively.
H. G. C.

Aromatic Alkyl Ketones and their Oxidation by Potassium Permanganate. By A. Claus (*J. pr. Chem.* [2], **43**, 138—147; compare Abstr., 1890, 769, 979; this vol., p. 199).—*Paracymylcarboxylic acid* [Me : COOH : Pr = 1 : 2 : 4] is obtained by slowly oxidising paracymylglyoxylic acid (this vol. p. 199) with acid solution of potassium permanganate, and separating the product by sublimation with steam as soon as possible to prevent further oxidation; it crystallises in small, colourless needles, melts at 69° (uncorr.), and sublimes.

Metaxylyl ethyl ketone [Me : COEt : Me = 1 : 2 : 5] is a colourless, aromatic, refractive liquid which boils at 238—239° (uncorr.). It dissolves in most solvents except water, is slightly volatile with steam, and does not solidify at −10°. The *phenylhydrazide* forms colourless leaflets which melt at 126° (uncorr.) and dissolve in hot water, alcohol, ether, and glacial acetic acid.

Metaxylylglyoxylic acid [Me_2 : CO·COOH = 1 : 5 : 2] (Abstr., 1886, 463), obtained by oxidising the ketone with permanganate, crystallises in long, flat prisms (with $\frac{1}{2}$ mol. H_2O) when hydrochloric acid is added to a hot dilute aqueous solution of its salts, and can be recrystallised in the same form (with $\frac{1}{2}$ mol. H_2O) from a mixture of chloroform and light petroleum; these crystals melt at 53—54° (uncorr.). But if hydrochloric acid is added to the solution of the salt in the cold, the glyoxylic acid separates as an oil which soon solidifies to a crystalline mass melting at 85° (uncorr.). The *barium* salt crystallises with 2 mols. H_2O; the *calcium* salt with 2 or $4\frac{1}{2}$ mols. H_2O, according to the conditions; the *sodium* salt crystallises from aqueous alcohol with 6 mols. H_2O, and from water with $1\frac{1}{2}$ mols.; the *potassium* salt crystallises with 1 mol. H_2O from water, and with varying amounts of H_2O from aqueous alcohol. When reduced with sodium amalgam, this acid yields *metaxylylglycollic acid* [Me_2 : CH(OH)·COOH = 1 : 5 : 2]; it crystallises from hot water in colourless, transparent rhombohedra, and from a mixture of chloroform and light petroleum in leaflets; it melts at 119° (uncorr.), and sublimes in small, lustrous rhombohedra.

Paraxylyl ethyl ketone has been already described (Abstr., 1887, 253); its oxidation does not produce paraxylyl-β-ketonic acid (*loc. cit.*), but paraxylylglyoxylic acid (Abstr., 1885, 1136), the so-called β-ketonic acid previously obtained being probably a mixture of the glyoxylic acid with xylylcarboxylic acid. Paraxylylglycollic acid (paraxylylhydroxyacetic acid, *loc. cit.*) crystallises in lustrous, colourless needles and prisms which melt at 114° (uncorr.), and dissolve in hot water, alcohol, ether, chloroform, and glacial acetic acid.
A. G. B.

Bromonitrobenzoic Acids. By A. Claus and W. Scheulen (*J. pr. Chem.* [2], **43**, 200—207; compare Abstr., 1888, 594; 1889, 987, 988).—*Metabromoparanitracetanilide* [Br : NO_2 : NH_2Ac =

3 : 4 : 1], obtained by nitrating metabromacetanilide, crystallises in broad, nearly colourless needles. *Metabromorthonitracetanilide* [$Br : NO_2 : NH_2Ac = 3 : 6 : 1$], which is obtained at the same time, forms colourless needles and melts at 139°; it dissolves in chloroform and ether, whereby it is separated from the metapara-compound.

Metabromoparanitraniline [$Br : NO_2 : NH_2 = 3 : 4 : 1$], obtained by de-acetylising the acetanilide with sulphuric acid, crystallises in lustrous, yellow, stellate needles; it melts at 172° (uncorr.), and is soluble in alcohol, but insoluble in chloroform, benzene, light petroleum, and, nearly so, in water.

Metabromoparanitrobenzonitrile [$Br : NO_2 : CN = 3 : 4 : 1$], obtained by means of the diazo-compound, forms colourless needles, and melts at 104° (uncorr.); it dissolves easily in benzene and in hot water.

Metabromoparanitrobenzoic acid [$Br : NO_2 : COOH = 3 : 4 : 1$], obtained by heating the nitrile with sulphuric acid, crystallises in long, colourless needles, melts at 197° (uncorr.), and dissolves sparingly in cold water, but freely in other solvents. The *sodium*, *potassium* (with 2 mols. H_2O), *barium* (with $\frac{1}{2}$ mol. H_2O), *lead* (with 1 mol. H_2O), *silver*, and *copper* salts are described.

Parabromorthonitrobenzonitrile [$Br : NO_2 : CN = 4 : 2 : 1$] crystallises in yellowish needles, melts at 99° (uncorr.), sublimes without decomposition, and dissolves in hot water and other solvents.

Parabromorthonitrobenzoic acid [$Br : NO_2 : COOH = 4 : 2 : 1$] crystallises in large, lustrous, transparent, colourless, columnar needles which melt at 163° (uncorr.), and dissolve freely in most solvents, except cold water. The *sodium*, *potassium*, *ammonium*, *calcium* (with 2 mols. H_2O), *barium*, *lead* (with 1 mol. H_2O), *copper* (with 7 mols. H_2O), and *silver* salts are described.

Parabromorthamidobenzoic acid [$Br : NH_2 : COOH = 4 : 2 : 1$] crystallises in long, colourless, strongly refractive needles which melt at 222° (uncorr.), and are easily soluble in alcohol, ether, and chloroform. The *barium* (with 1 mol. H_2O), *calcium* (with $\frac{1}{2}$ mol. H_2O), and *silver* salts are described. A. G. B.

New Mode of Formation of Benzoic Anhydride. By G. Minunni and L. Caberti (*Gazzetta*, **20**, 655—656).—A mixture of freshly-distilled benzoic chloride (50 grams) and fused and powdered sodium nitrite (150 grams) is heated for about 12 hours on the water-bath, the product extracted with dry ether, and freed from traces of benzoic acid by rapidly washing with a very dilute solution of sodium carbonate, and then with distilled water. The crude product is very pure. When dried in a vacuum, it melts at 42—43°. The yield is 74 per cent. Acetic chloride similarly treated with sodium nitrite is largely resinified: a small amount of acetic anhydride may, however, be extracted. The reaction is probably $2BzCl + 2NaNO_2 = Bz_2O + 2NaCl + N_2O_3$. S. B. A. A.

New Method for Obtaining Aromatic Carboxylic Acids. By H. Frey and M. Horowitz (*J. pr. Chem.* [2], **43**, 113—124).—The aromatic hydrocarbon is heated with a fatty acid, zinc chloride, and phosphorus oxychloride.

Toluene (1 part), glacial acetic acid (2 parts), and granulated zinc chloride (2 parts) are heated in a reflux apparatus at 105—110°; when the zinc chloride has dissolved, phosphorus oxychloride (1 part) is added by degrees through the condenser, the flask being shaken meanwhile; the temperature is now raised to 115—120° and kept at that until the mixture has become greenish-black and ceases to evolve large bubbles of hydrogen chloride. The product is then mixed with much water, whereby a resin is separated from which the paratoluic acid is extracted with 5 per cent. aqueous soda; the yield is 30—35 per cent. of the toluene. Methyl tolyl ketone (Abstr., 1882, 970) is obtained at the same time, but only in small quantity, unless the heating is discontinued while much hydrogen chloride is coming off; the product is then distilled with steam and the ketone extracted from the distillate by ether. Methyl chloride is evolved during the reaction, and the authors are thus led to the following explanation:—

(1.) $C_6H_5Me + Me{\cdot}COOH = C_6H_4Me{\cdot}COMe + H_2O$.
(2.) $C_6H_4Me{\cdot}COMe + POCl_3 = C_6H_4Me{\cdot}CO{\cdot}POCl_2 + MeCl$.
(3.) $C_6H_4Me{\cdot}CO{\cdot}POCl_2 + 3H_2O = C_6H_4Me{\cdot}COOH + H_3PO_3 + 2HCl$.

By the same method, metaxylene and acetic acid yielded orthoparaxylic acid [$COOH : Me_2 = 1 : 2 : 4$], which was found to melt at 122°, thus confirming Kekulé and Hepp, and controverting others who give the melting point as 126°; on nitration, it yielded a dinitroxylic acid melting at 197°. Orthoparadimethylacetophenone (b. p. 224—225° under a pressure of 715 mm.; compare Claus, Abstr., 1886, 463) can also be prepared (25 per cent.) by this method; a tribromoderivative melting at 69° was obtained.

Paraxylene yielded the xylic acid [$COOH : Me_2 = 1 : 2 : 5$] melting at 132° (Abstr., 1882, 187), and orthoxylene the acid [1 : 3 : 4] melting at 163°. These and other experiments show that the method is a general one. A. G. B.

Cumarone. By D. Bizzarri (*Gazzetta*, **20**, 607—611).—Cumarone, prepared by the dry distillation of cumarilic acid with lime according to Fittig and Ebert's method (Abstr., 1883, 474), is a colourless liquid boiling at 169°, which powerfully resists the action of heat and reagents. It is not altered by heating to redness with quicklime and ammonium chloride. It is not affected by aqueous or alcoholic ammonia, even after prolonged heating at 140°; aniline alone has no action on it, even after heating for 40 hours at 230—250°, but the addition of sulphuric acid effects a condensation of the two compounds—a reddish resin being formed. When heated with aniline and zinc chloride at 220°, a brown mass is formed consisting of various impure products, a reddish-yellow, semitransparent resin—probably Kraemer and Spilker's paracumarone, and, lastly, a compound crystallising from benzene in pale yellowish plates soluble in alcohol and ether and giving in alcoholic solution a yellow *picrate* and a white, flocculent *hydrochloride*. The latter darkens on exposure to the air, and has approximately the composition of amidophenanthrene hydrochloride.

When the crystals are dissolved in concentrated sulphuric acid, nitrous fumes passed into the solution, and the product thrown into boiling absolute alcohol, aldehyde is evolved, and the residue contains a small quantity of phenanthrene. If the crystals are directly oxidised by chromic acid, amidophenanthraquinone is obtained.

S. B. A. A.

Condensation Products of Anilidoglutaric Acid. By A. Reissert (*Ber.*, **24**, 314—320).—Some time ago the author described two substances, namely, pyranilpyroïnlactone and phenylketoxydimethylanilidotetrahydropyridinecarboxylic lactone, which he obtained by heating anilidoglutaric acid at 170—180° until the evolution of gas was at an end (compare Abstr., 1888, 694; 1889, 1174). Anschütz (Abstr., 1890, 774) came to the conclusion that pyranilpyroïnlactone is identical with citraconanil, because when anilidoglutaric acid is distilled under reduced pressure, it yields citraconanil only. The author has repeated his experiments, and finds that the two substances described by him are in fact obtained when anilidoglutaric acid is heated at 170—180°, but that they are not definite chemical compounds. Pyranilpyroïnlactone is a mixture of citraconanil and the second condensation product of anilidoglutaric acid. Pyranilpyroïnlactonic acid (*loc. cit.*) is a mixture of mesaconanilic acid with the acid (m. p. 150°) previously described (*loc. cit.*).

Phenylketoxydimethylanilidotetrahydropyridinecarboxylic lactone is simply anilidoglutaranil, so that the names and constitutional formulæ assigned to all the derivatives of this compound, which have been previously described, must be altered. F. S. K.

Metadinitrodiphenyldisulphine. By A. Ekbom (*Ber.*, **24**, 335—338).—*Metadinitrodiphenyldisulphine*, $NO_2{\cdot}C_6H_4{\cdot}SO{\cdot}SO{\cdot}C_6H_4{\cdot}NO_2$, is obtained by heating metanitrobenzenesulphonic chloride, dissolved in acetic acid, with the calculated quantity of hydriodic acid (sp. gr. = 1·5) for 2½ hours on the water-bath. The product is treated with water, the precipitate washed with alcohol, and then crystallised from alcohol. The yield is about 50 per cent. of that required by theory. It crystallises in rhombohedral prisms or beautiful needles, melts at 124°, is easily soluble in acetic acid and hot alcohol, sparingly in cold alcohol and light petroleum, and insoluble in water. When heated in acetic acid solution on the water-bath with hydriodic acid (sp. gr. = 1·5), or with sulphurous acid, it is reduced to metadinitrodiphenyl bisulphide. The latter crystallises from alcohol in needles or rhombic tablets, and melts at 84°. E. C. R.

Substituted Sulphones. By W. Autenrieth (*Ber.*, **24**, 166—172; compare E. Stuffer, this vol., p. 180).—*Thioethylacetone ethylmercaptole*, $SEt{\cdot}CH_2{\cdot}CMe(SEt)_2$, is obtained by the action of hydrogen chloride on a mixture of thioethylacetone (1 mol.) with ethyl mercaptan (2 mols.); it is a yellow, oily liquid which decomposes on distillation. On treatment with potassium permanganate, the corresponding trisulphone, $SO_2Et\cdot CH_2\cdot CMe(SO_2Et)_2$, is formed, from which the author was unable to prepare a methyl derivative.

Thiophenylacetonediethylmercaptole, $SPh\cdot CH_2\cdot CMe(SEt)_2$, from thiophenylacetone and ethyl mercaptan, is a yellow, viscid liquid which cannot be distilled. The *trisulphone*, $SO_2Ph\cdot CH_2\cdot CMe(SO_2Et)_2$, solidifies with difficulty, crystallises from alcohol in lustrous plates, melts at 127—128°, and is insoluble in water. On heating it with normal potash solution for three hours in a reflux apparatus, the three sulphone groups are eliminated.

Thioethylacetonediphenylmercaptole, $SEt\cdot CH_2CMe(SPh)_2$, from thioethylacetone and phenyl mercaptan, resembles the preceding compounds; no trisulphone could, however, be obtained from it.

Thiophenylacetonediphenylmercaptole, $SPh\cdot CH_2\cdot CMe(SPh)_2$, prepared from thiophenylacetone and phenyl mercaptan, crystallises from alcohol in cubic crystals, melts at 54—55°, and dissolves readily in ether, but is insoluble in water. No corresponding trisulphone could be obtained.

Chloracetonediethylmercaptole, $CH_2Cl\cdot CMe(SEt)_2$, is formed by the action of chloracetone on ethyl mercaptan. It is a colourless oil which is volatile with steam, and on oxidation yields *diethylsulphonechlorodimethylmethane*, $CH_2Cl\cdot CMe(SO_2Et)_2$; this crystallises from water in small, white, lustrous plates, melts at 78—79°, and is readily soluble in alcohol, ether, or chloroform; by treatment with potash, it is completely hydrolysed; the chlorine atom appears to be very firmly linked in the molecule, since all attempts to replace it have hitherto been unsuccessful. J. B. T.

Phenylsulphoneacetonemercaptole. By R. OTTO and A. RÖSSING (*Ber.*, **24**, 234—237).—It has already been shown by R. and W. Otto (Abstr., 1888, 282) that phenylsulphoneacetone is converted by treatment with thiophenol in presence of a dehydrating agent into phenylsulphoneacetonediphenylmercaptole,

$$SO_2Ph\cdot CH_2\cdot COMe + 2PhSH = H_2O + SO_2Ph\cdot CH_2\cdot CMe(SPh)_2.$$

By the oxidation of the latter with potassium permanganate, an insoluble product is obtained, which appears to consist of *thiophenyldiphenylsulphonepropane*, $SO_2Ph\cdot CH_2\cdot CMe(SPh)\cdot SO_2Ph$. It is a granular, crystalline compound melting at 148—149°, and sparingly soluble in alcohol. On further oxidation, it is converted into benzenesulphonic acid, which is therefore also found in large quantity in the original oxidation product.

Aqueous potash quickly converts the mercaptole into methylphenylsulphone, thiophenol, and acetic acid, but it is not attacked by reducing agents in acid solution. H. G. C.

Benzenesulphonates of Aromatic Radicles. By M. GEORGESCU (*Ber.*, **24**, 416—418).—Benzenesulphonic chloride acts on dilute alkaline solutions of phenols in the same manner as on other hydroxy-compounds (this vol., pp. 49, 202), forming salts of benzenesulphonic acid. *Phenyl benzenesulphonate*, $C_6H_5\cdot SO_3Ph$, obtained from phenol, forms colourless crystals, and melts at 35—36° (see also following abstract). It is a very stable compound, and is not attacked by an acetic acid solution of hydrogen chloride at 160°, and only with difficulty by hot alcoholic potash.

β-Naphthyl benzenesulphonate, $C_6H_5{\cdot}SO_3{\cdot}C_{10}H_7{}^{\beta}$, prepared from β-naphthol, also forms colourless crystals, and melts at 105—107°. *Cymyl benzenesulphonate*, $C_6H_5{\cdot}SO_3{\cdot}C_6H_3MePr^{\beta}$, is a pulverulent precipitate, but may be obtained from hot alcohol in needles melting at 55—56°. *Resorcinyl phenylsulphonate*, $C_6H_4(O{\cdot}SO_2Ph)_2$, crystallises from hot alcohol in needles, and melts at 67—70°; the *quinol* derivative, $C_6H_4(O{\cdot}SO_2Ph)_2$, forms pale, yellowish crystals, and melts at 120—121°; the *pyrogallol* and *phloroglucinol* derivatives, $C_6H_3(O{\cdot}SO_2Ph)_3$, both separate from alcohol in colourless crystals melting at 140—142° and 115—117° respectively. All these compounds are soluble in hot alcohol, benzene, chloroform, and carbon bisulphide, but only dissolve sparingly in ether. H. G. C.

Benzenesulphonates of Aromatic Radicles. By R. OTTO (*Ber.*, **24**, 643—644).—In connection with Georgescu's paper on this subject (preceding abstract), the author points out that five years ago he obtained phenyl benzenesulphonate and some of its homologues, and published an account of their chemical and crystallographical properties (Abstr., 1886, 883). H. G. C.

Aromatic Sulphonamic Acids. By W. TRAUBE (*Ber.*, **24**, 360—364; compare Abstr., 1890, 1137).—On adding 1 molecular proportion of aniline to a solution of chlorosulphonic acid in chloroform, aniline chlorosulphonate is probably formed; the further addition of aniline causes the production of aniline phenylsulphonamate. This substance is also obtained, together with aniline sulphate, by the action of fuming sulphuric acid on aniline at low temperatures; it thus appears probable that the formation of sulphanilic acid is preceded by that of phenylsulphonamic acid.

Barium dibromophenylsulphonamate, $(C_6H_3Br_2{\cdot}NH{\cdot}SO_3)_2Ba$, is prepared by the action of bromine-water on barium phenylsulphonamate, and crystallises from dilute ammonia; on treatment with acids, it yields dibromaniline and sulphuric acid.

Sulphanilide, $SO_2(NHPh)_2$, was the only compound that could be obtained by the action of phosphorus pentachloride or phosphorus oxychloride on phenylsulphonamic acid; it is very sparingly soluble in water, but dissolves in alkalis, and is not affected by acids.

Ammonium methylphenylsulphonamate, $NMePh{\cdot}SO_3NH_4$, is prepared from chlorosulphonic acid and methylaniline in the manner already described (*loc. cit.*); the *potassium salt* forms a crystalline powder.

Ammonium diphenylsulphonamate is very unstable.

Ammonium β-naphthylsulphonamate is deposited from water in colourless crystals which slowly become red on exposure to air.

Diamylsulphonamic acid, $N(C_5H_{11})_2{\cdot}SO_3H$, is prepared from chlorosulphonic acid and diamylamine; it crystallises from alcohol, and melts at 98°. The compound is not affected by boiling with water or dilute acids, but is decomposed by concentrated acids. The stability of the sulphonamic acids is therefore decreased by the presence of aromatic groups; compounds containing two aromatic radicles decompose even in alkaline solution, whilst those with only one yield crystalline salts. J. B. T.

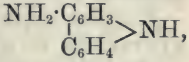
Orthodinitrodiphenyl and Orthodiamidodiphenyl. By E. Täuber (*Ber.*, **24**, 197—201).—2 : 6′-*Orthodinitrodiphenyl*, $C_{12}H_8(NO_2)_2$ $[(NO_2)_2 = 2 : 2']$, is prepared by the action of ethyl nitrite on metadinitrobenzidine hydrochloride; it crystallises from alcohol in straw-coloured needles, melts at 124°, and is readily soluble in benzene and glacial acetic acid, but only very sparingly in light petroleum. On reduction with tin and hydrochloric acid, *orthodiamidodiphenyl*, $C_{12}H_8(NH_2)_2$, is formed, crystallising from dilute alcohol in small, colourless needles, and melting at 81°; in small quantities, it may be distilled without composition. The *hydrochloride* and *sulphate* are crystalline, and readily soluble in water or dilute alcohol.

The amide yields a *tetrazo*-derivative, which has only very feeble tinctorial properties; on boiling the chloride with water, a substance is obtained which is probably impure diphenylene oxide.

The *diacetyl derivative* of diamidodiphenyl crystallises from absolute alcohol in small, colourless prisms melting at 161°.

Carbazole is obtained by heating orthodiamidodiphenyl with six parts of dilute (25 per cent.) sulphuric acid in a sealed tube for 15 hours at 200°; an equivalent quantity of 15 per. cent. hydrochloric acid may also be employed. J. B. T.

Carbazole. By G. Mazzara (*Ber.*, **24**, 278—281).—*Benzoylcarbazole*, $C_{12}H_8N\cdot COPh$, is formed when carbazole is heated with excess of benzoic chloride at 160—170° for two hours. It crystallises from boiling alcohol in greenish needles, melts at 98·5°, is volatile with steam, and is moderately easily soluble in ether, but only sparingly in benzene and light petroleum; it dissolves in glacial acetic acid yielding a green solution, and is decomposed by alcoholic potash into carbazole and benzoic acid. It is not acted on by phenylhydrazine in boiling alcoholic solution, but hydroxylamine, under the same conditions, decomposes it, and carbazole is produced. The *nitro*-compound, $NO_2\cdot C_{12}H_7N\cdot COPh$, can be prepared by gradually adding nitric acid of sp. gr. 1·48 (18 grams), to a lukewarm glacial acetic acid solution of benzoylcarbazole (9 grams), and then heating the mixture on the water-bath for a few minutes. It crystallises from boiling glacial acetic acid in yellow plates, melts at 181°, and is soluble in warm ether and benzene, but only sparingly in alcohol and light petroleum; it is not acted on by boiling potash, but boiling 6 per cent. alcoholic potash slowly converts it into *nitrocarbazole*, $C_{12}H_8N_2O_2$. This compound crystallises from boiling alcohol in plates, melts at 210° to a red liquid, and is only sparingly soluble in warm glacial acetic acid, chloroform, and benzene, and almost insoluble in ether and light petroleum. F. S. K.

Carbazole Syntheses. By A. Blank (*Ber.*, **24**, 306).—Carbazole is formed in considerable quantity when the vapour of orthamidodiphenyl is passed over heated lime. *Amidocarbazole*,  $\left.\begin{matrix}NH_2\cdot C_6H_3\\ | \\ C_6H_4\end{matrix}\right>NH$, can be obtained from diphenyline in like manner; it crystallises from water in small, slender needles melting at 238°. F. S. K.

Condensation of Unsaturated Hydrocarbons with Phenols. Tetrahydronaphthylphenol. By W. Koenigs (*Ber.*, **24**, 179—181; compare this vol., p. 208). *Tetrahydronaphthylphenol*, $C_{10}H_{11}\cdot C_6H_4\cdot OH$, is prepared by the action of equal parts of concentrated sulphuric acid and glacial acetic acid on a mixture of phenol and dihydronapthalene; after purification, the compound crystallises from a mixture of ether and light petroleum, or from dilute alcohol, in aggregates of needles; it melts at 129—130° with previons softening, and boils at 320° without decomposition. It is readily volatile with steam at 160°, but more slowly at 100°; no characteristic coloration is obtained with ferric chloride; the yield is 70 per cent. of the dihydronaphthalene employed.

The phenol may also be obtained by the action of sulphuric acid alone, but the product appears to be less pure. The *sodium salt* is formed as a flocculent, crystalline precipitate on cooling a solution of the phenol in soda. The *benzoyl* derivative crystallises from absolute alcohol, and melts at 107—108°. J. B. T.

Picryl-α- and β-naphthylhydrazines, and α-Dinitrophenyl-α-, and β-naphthylhydrazines and their Derivatives. By C. Willgerodt and F. Schulz (*J. pr. Chem.* [2], **43**, 177—189).—The picrylnaphthylhydrazines are prepared by the action of alcoholic solutions of picryl chloride on the naphthylhydrazine (obtained after E. Fischer, Abstr., 1886, 554), or its hydrochloride (equal mols.); they exist in a stable and an unstable form.

Picryl-α-naphthylhydrazine.—The *red* or *stable* modification of this compound is obtained if the reaction is assisted by heat, and crystallises, as the mixture cools, in short, dark-brown prisms; it can be purified by washing with water. It decomposes at 176°, dissolves in most organic solvents, and is indifferent in its behaviour to acids and alkalis. The *yellow* or *unstable* modification is amorphous, and is formed if the reaction takes place in the cold; it must be quickly filtered, and dried on a porous plate, as it rapidly changes into the red modification if left in the mother liquor, and even more quickly when heated with solvents; when heated by itself, the change occurs at 140°.

Picryl-β-naphthylhydrazine.—Both modifications are obtained in the same way as those of the α-compound. The *red*, or *stable*, modification crystallises in red prisms which decompose at 175°; it is sparingly soluble in alcohol and ether, but easily in chloroform, glacial acetic acid, benzene, and acetone. The *yellow*, or *unstable*, modification is amorphous, and so unstable that it is impossible to prepare it quite free from the red modification, into which it passes, when heated alone at 100°, or with solvents. It is suggested that these stable and unstable forms are stereochemical isomerides.

Picrylazonaphthalenes are obtained by adding the corresponding hydrazines to a warm solution of excess of chromic acid in acetic acid; the mixture is then poured into water, and the precipitate washed with water. *Picryl-α-azonaphthalene* crystallises from glacial acetic acid in red-yellow needles which melt and decompose at 226°; it dissolves sparingly in benzene and alcohol. *Picryl-β-azonaphthalene* crystallises in dull-red needles, melts at 205° with decomposition, and dissolves easily in glacial acetic acid, but sparingly in alcohol and benzene.

Dinitronitrosophenyl-α-azonaphthalene is obtained by heating picryl-α-naphthylhydrazine with glacial acetic acid in a reflux apparatus until the colour of the crystals, which separate on cooling, is quite yellow; it forms yellow needles, melts at 232°, and dissolves easily in benzene, but more sparingly in glacial acetic acid and alcohol.

Dinitronitrosophenyl-β-azonaphthalene, similarly prepared, crystallises in yellow leaflets, melts at 245° with decomposition, and dissolves easily in glacial acetic acid, but more sparingly in alcohol, ether, and benzene; it dissolves in strong sulphuric acid with a brilliant dark-blue colour, which becomes greenish-yellow on dilution with water.

Dinitrosonitrophenyl-α-azonaphthalene is prepared by heating picryl-α-naphthylhydrazine with alcohol in a sealed tube, for 2—3 hours at 120°, dissolving the product in benzene, and decolorising with animal charcoal; it crystallises in slender, yellowish-brown needles, melts at 210°, and is moderately soluble in benzene and glacial acetic acid, but less so in alcohol.

Dinitrosonitrophenyl-β-azonaphthalene is obtained by heating picryl-β-naphthylhydrazine with alcohol in a reflux apparatus for 14 hours; it melts at 231° with partial decomposition, and dissolves in hot glacial acetic acid and benzene, but hardly at all in alcohol.

Orthoparadinitrophenyl-α-naphthylhydrazine is obtained by dissolving phenyl-α-naphthylhydrazine (4 grams), in alcohol, adding α-dinitrochlorobenzene (2·56 grams), and heating in a reflux apparatus for $\frac{1}{2}$—$\frac{3}{4}$ hour; the crystalline mass which separates on cooling is purified by heating with dilute hydrochloric acid. It crystallises from benzene in long, narrow, red prisms, melts at 181°, and dissolves sparingly in alcohol.

Orthoparadinitrophenyl-β-naphthylhydrazine, similarly prepared, crystallises in short, reddish-yellow prisms, melts at 188° with decomposition, and dissolves sparingly in alcohol and benzene, but more freely in glacial acetic acid, in which it is unstable.

Orthoparadinitrophenyl-α-azonaphthalene, obtained by heating the corresponding naphthylhydrazine with excess of chromic acid in acetic acid and pouring the mixture into water, crystallises in slender, reddish-brown needles, melts at 190°, and dissolves sparingly in alcohol, and more freely in glacial acetic acid and benzene.

Orthoparadinitrophenyl-β-azonaphthalene, similarly prepared, crystallises in reddish-yellow needles, melts at 178°, and dissolves in glacial acetic acid.

Orthoparanitronitrosophenyl-α-azonaphthalene is prepared by heating orthoparadinitrophenyl-α-naphthylhydrazine with glacial acetic acid in a reflux apparatus for two hours; it crystallises in green needles, melts at 201°, and dissolves in glacial acetic acid and benzene, but only sparingly in alcohol.

Orthoparanitronitrosophenyl-β-azonaphthalene, similarly obtained, crystallises in yellow needles, melts at 225°, and dissolves in glacial acetic acid, but only sparingly in alcohol and benzene.

Orthoparadinitrosophenyl-α-azonaphthalene is obtained by heating orthoparadinitrophenyl-α-naphthylhydrazine with alcohol in a sealed tube for six hours at 120°, cooling, and heating the crystals with glacial acetic acid and animal charcoal; it is yellow, amorphous, and melts at 162°.

Orthoparadinitrosophenyl-β-azonaphthalene is prepared in a similar manner; after long heating with glacial acetic acid, it forms microscopic, yellow needles; it melts at 178°, and dissolves in glacial acetic acid and benzene, but only sparingly in alcohol.

The molecular weights of the foregoing compounds have been checked by Raoult's method. A. G. B.

Action of Hydriodic Acid on 1—3′-Nitronaphthalenesulphonamide. By A. EKBOM (*Ber.*, **24**, 329—335).—The action of hydriodic acid on 1—3′-nitronaphthalenesulphonamide is similar to its action on the 1—4′-compound (Abstr., 1890, 994).

Amidonaphthalenesulphonamide [$NH_2 : SO_2NH_2 = 1 : 3'$] is prepared by heating nitronapthalenesulphonamide with excess of hydriodic acid (sp. gr. = 1·5) and red phosphorus for seven hours; the product is dissolved in alcohol, treated with sulphurous acid, and ammonia added until an alkaline reaction is obtained, when the amide is precipitated as a yellow, crystalline compound. It crystallises from alcohol in slender, silky needles, melts at 218—219° with carbonisation, and is easily soluble in hot alcohol, sparingly in cold, and insoluble in water. The *hydrochloride*, obtained by dissolving the amide in hydrochloric acid, crystallises in scales. The *hydriodide* crystallises from concentrated alcoholic hydriodic acid in beautiful, pale-yellow needles. The *sulphate* crystallises in prisms. *Acetamidonaphthalenesulphonamide* is obtained by treating the above compound with excess of acetic anhydride; it crystallises from alcohol in small aggregates consisting of radiating, light-red needles, and melts at 238—239°. An attempt to prepare the diacetyl compound by heating amidonaphthalenesulphonamide in a sealed tube with excess of acetic anhydride for 2½ hours at 156° failed. The author draws attention to the fact that Cleve obtained a monacetyl derivative from the 1 : 3 and 1 : 2′-amidonaphthalenesulphonamides and a diacetyl derivative from the 1 : 4-compound, and that he has obtained a diacetyl derivative from the 1 : 4′-compound. Hence if the group SO_2NH_2 be in a β-position, a monacetyl compound is obtained; if it be in an α-position, a diacetyl-compound is formed.

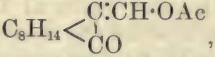
1 : 3′-Diamidodinaphthyl bisulphide, $NH_2{\cdot}C_{10}H_6{\cdot}S{\cdot}S{\cdot}C_{10}H_6{\cdot}NH_2$, is prepared by treating 1 : 3′ nitronaphthalenesulphonamide with excess of hydriodic acid (sp. gr. = 1·96), and when the reaction is ended,

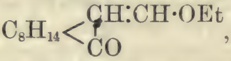
boiling the mixture gently for three hours. The product is dissolved in alcohol, treated with sulphurous acid and ammonia, and the precipitate washed with water and crystallised from alcohol several times. It crystallises in pale-yellow needles, melts at 166°, and is easily soluble in alcohol, ether, benzene, and acetic acid, sparingly in light petroleum, and insoluble in water. The same bisulphide was obtained by reducing the dinitrodinaphthyl bisulphide from the β-acid (Abstr., 1888, 698) with hydriodic acid and phosphorus. The *hydrochloride*, $NH_2\cdot C_{10}H_6\cdot S\cdot S\cdot C_{10}H_6\cdot NH_2,2HCl$, is obtained as a white precipitate on adding hydrochloric acid to an alcoholic solution of the diamide; on boiling with water, it is decomposed into hydrochloric acid and diamidodinaphthyl bisulphide. The *hydriodide* is obtained in yellow needles on concentrating an alcoholic solution of the diamide, saturated with hydriodic acid. *Diacetodiamidodinaphthyl bisulphide*, obtained by treating diamidodinaphthyl bisulphide with excess of acetic anhydride, crystallises from acetic acid in colourless, microscopic needles, and melts at 276° with carbonisation.

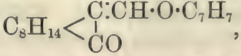
When 1 : 3′-nitronaphthalenesulphonamide and 1 : 3′-diamidodinaphthyl bisulphide are treated with excess of hydriodic acid (sp. gr. = 1·96), and the mixture boiled briskly for 3—4 hours, a product is obtained, somewhat easily soluble in alcohol, which, after treatment with ammonia, forms a viscid, evil-smelling substance; the author assumes it to be β-amidothionaphthol.

E. C. R.

Action of Ethyl Formate on Camphor. By L. CLAISEN (*Chem. Centr.*, 1890, ii, 878—880; from *Sitzber. math.-naturw.*, *Abt. bayr. Akad. Wiss.*, 1890, 445—479).—*Formylcamphor*, the preparation of which has been already described (Abstr., 1888, 692 and 1889, 619), melts at 76—78°, boils at 240—243° under 760 mm. pressure, and at 138° under 28 mm. pressure. It behaves as a fairly strong acid and liberates acetic acid from its salts; ferric chloride produces a dark violet-red coloration in its alcoholic solution; the *ferric salt* is nearly black, crystalline, insoluble in water, soluble in alcohol, ether, benzene, and chloroform forming a dark red solution; the *copper salt*, $(C_{11}H_{15}O_2)_2Cu + 2C_{11}H_{16}O_2$, melts at 126° and crystallises from light petroleum in silky, lustrous needles.

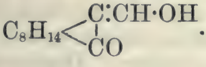
Acetylformylcamphor,  $C_8H_{14}<\begin{matrix}C{:}CH\cdot OAc\\ |\\ CO\end{matrix}$, melts at 60—62° and boils at 175—177°; it gives no coloration with ferric chloride.

Ethylformylcamphor,  $C_8H_{14}<\begin{matrix}CH{:}CH\cdot OEt\\ |\\ CO\end{matrix}$, is a colourless oil, which boils at 266—268° under 760 mm. pressure, sp. gr. 1·006 at 15°; it is insoluble in water and dilute alkalis. With ferric chloride, it produces no coloration (unless decomposed), and is decomposed by hydrogen bromide into alcohol and formylcamphor.

Benzylformylcamphor,  $C_8H_{14}<\begin{matrix}C{:}CH\cdot O\cdot C_7H_7\\ |\\ CO\end{matrix}$, melts at 45—46°, and boils at 222—224° under a pressure of 16 mm. *Anilidoformyl-*

camphor, $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NHPh\\ |\\ CO\end{array}$, melts at 156—159°, and is prepared by the action of aniline either on a methyl alcohol solution of formylcamphor or on ethylformylcamphor. *Methylanilidoformylcamphor*, $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NMePh\\ |\\ CO\end{array}$, melts at 124° and separates from its solution in chloroform and light petroleum in beautiful crystals of the rhombic system, $a : b : c = 0{\cdot}792 : 1 : 0{\cdot}7535$. The *monhydrazone* of *camphorquinone* melts at 169—170°.

From a consideration of the properties and reactions of formylcamphor, the author considers that it has the formula



$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot OH\\ |\\ CO\end{array}.$$

Menthone appears to react with ethyl formate in a similar manner to camphor. J. W. L.

Influence of Solvents on the Rotatory Powers of Camphols and Isocamphols: Chloral Borneolates. By A. HALLER (*Compt. rend.*, **112**, 143—146).—The rotatory power of lævogyrate α-camphol is independent of the nature of the solvent, except in the case of methyl alcohol, when it is below its normal value; the effect of various solvents in the case of lævogyrate isocamphol varies with their nature, but is the same for members of a homologous series.

Chloral borneolates are obtained by direct union of borneol and anhydrous chloral at the ordinary temperature. The α-compounds crystallise, but the products from isocamphol and $+\alpha-\beta$-borneol are viscous and do not crystallise even at 15°. All the compounds have the formula $CCl_3\cdot CH(OH)\cdot OC_{10}H_{17}$, and are decomposed by boiling water into camphols and chloral hydrate. Their rotatory powers in a benzene solution containing half a gram-molecule per litre were as follows:—

	Melting point.	Molecular rotatory power.
Dextrogyrate chloral α-borneolate (cryst.)........................	55—56°	+30·13°
Lævogyrate chloral α-borneolate (cryst.)........................	55—56	−30·13
Racemic chloral borneolate $(-\alpha+\alpha)$ cryst.	55—56	0·0
Lævogyrate chloral isoborneolate or β-borneolate....................	—	−56·40°
Chloral $-\beta+\alpha$-borneolate from inactive $-\beta+\alpha$-camphol..........	—	−22·12

The differences between the various derivatives are of the same order as in the case of the bornylphenyl-urethanes. It is clear that the orientation of the elements of the group $H\cdot\dot{C}\cdot OH$ exerts an important influence on the rotatory power and other physical properties of these additive compounds. C. H. B.

Digitonin and Digitogenin. By H. Kiliani (*Ber.*, **24**, 339—347).—The author has shown in a former communication (Abstr., 1890, 996), that pure commercial digitalin, when heated with dilute hydrochloric acid, gives, besides dextrose and galactose, a large quantity of digitogenin, $C_{15}H_{24}O_3$.

Digitonin is best obtained from commercial digitalin by extraction with 85 per cent. alcohol. Digitalin (1 part) is dissolved in 85 per cent. alcohol (4 parts) at 50—60° and the solution allowed to crystallise slowly. The crude product thus obtained is dissolved in 12 times its weight of boiling alcohol (85 per cent.), heated for two minutes with animal charcoal, and filtered: by rubbing the sides of the beaker as the solution cools, the product is obtained in nodular aggregates of slender needles. The crystals are, however, more compact and the product purer if the solution is allowed to cool very slowly without rubbing the sides of the beaker. Digitonin crystallises easily from 85 per cent. alcohol, whilst from stronger alcohol it is only obtained in the amorphous state, begins to soften at 225°, is completely melted at 235°, and is lævo-rotatory; for a 2·8 per cent. solution in 75 per cent. acetic acid, $[\alpha]_D = -50°$. The amorphous digitonin of Schmiedeberg dissolved in cold water in all proportions; the crystalline substance is sparingly soluble in water; on heating, it dissolves more easily, but does not crystallise on cooling, and the solution always shows an opalescence. With concentrated sulphuric acid, it gives a red solution; the addition of a drop of bromine-water greatly intensifies the reaction. Concentrated hydrochloric acid gives a colourless solution which, after a time or on heating, turns yellow and then red. Heated with dilute hydrochloric acid under the same conditions as were before given for digitalin, it yields nearly the calculated quantities of digitogenin, dextrose, and galactose. The digitogenin obtained in this way was identical in every respect with that formerly obtained from digitalin.

Derivatives of Digitogenin.—When digitogenin is heated in a sealed tube with concentrated hydriodic acid and red phosphorus, a large quantity of a resin containing iodine is formed; but neither methyl nor ethyl iodide.

Acetyldigitogenin, $C_{15}H_{23}O_3Ac$, is obtained by heating digitogenin (1 part) with anhydrous sodium acetate (1 part) and acetic anhydride (6 parts) in a reflux apparatus for one hour, and pouring the bright red solution in a fine stream into a large quantity of water. It crystallises from a small quantity of absolute alcohol in beautiful needles, melts at 178°, and is extremely soluble in warm alcohol, ether, and acetic acid. Instead of sodium acetate, sulphuric acid can be employed as a condensing agent: when zinc chloride is employed, amorphous compounds which were not examined are obtained. The author points out that the formation of a monacetyl derivative from digitogenin, does not agree with the production of two sugars from digitonin, which latter fact points to the existence of two hydroxyl groups in digitogenin.

Digitogenin on oxidation yields, according to the conditions, three acids, which the author names respectively, digitogenic, oxydigitogenic, and digitic acids.

Digitogenic Acid, $C_{14}H_{22}O_4$, is prepared by slowly adding chromic acid (0·7 part dissolved in 1·4 parts of water and 7 parts of acetic acid) to a solution of digitogenin (1 part) in acetic acid (30 parts) As soon as all the chromic acid is reduced, an equal volume of water is added, and the mixture repeatedly extracted with ether. The ethereal solution is allowed to remain for 24 hours, poured off from the deposit which is formed, the ether distilled off, and the acid residue evaporated on the water-bath until a crystalline crust forms on the liquid; the product crystallises after 12 hours. The yield amounts to 60 per cent. of the digitogenin employed. It crystallises from absolute alcohol in colourless needles or thin prisms, begins to melt at 146°, and is completely melted at 150°, becomes strongly electric when rubbed, tastes extremely bitter, and is easily soluble in chloroform and hot glacial acetic acid, less easily in 50 per cent. acetic acid, more sparingly in cold alcohol and ether, and insoluble in water; when heated with water, it melts. When moistened with dilute alcohol, it has a distinctly acid reaction. It dissolves easily in alkali hydroxides and carbonates. The *magnesium salt* $(C_{14}H_{21}O_4)_2Mg$, prepared by adding an excess of dilute magnesium nitrate (1 : 10) to a very dilute neutral solution of the acid, separates as a crust consisting of aggregates of minute needles on allowing the mixture to remain for 24 hours. The *calcium* salt is similar to the magnesium salt. The bye-products of the oxidation with chromic acid probably contain formaldehyde or formic acid, as no evolution of carbonic anhydride was observed. The mother liquors contained a small quantity of an aldehydic or ketonic compound and a large quantity of an acid of high molecular weight which yields no crystalline derivatives.

Oxydigitogenic acid, $2C_{14}H_{20}O_4 + H_2O$, is prepared by dissolving digitogenic acid (1 part) in potash (1 : 10) (10 parts), diluting the solution to 100 parts, and adding a solution of potassium permanganate (1 : 50). When the oxidation is finished, the solution is decolorised with a few drops of alcohol, filtered, one-third the weight of 93 per cent. alcohol added, and the acid precipitated with 50 per cent. acetic acid. In this way it is obtained crystallised in nodular aggregates of needles, which begin to melt at 250°; it is very sparingly soluble in alcohol and acetic acid, and becomes strongly electric when rubbed. The yield amounts to 70 per cent. of the digitogenic acid employed. The *magnesium* salt, $(C_{14}H_{19}O_4)_2Mg$, is very sparingly soluble and crystallises in aggregates of small needles.

Digitic acid, $C_{10}H_{16}O_4$, is formed, together with oxydigitogenic acid, by the oxidation with permanganate of digitogenic acid dissolved in 3 parts of potash. When the oxidation is ended, the solution is decolorised with a few drops of alcohol, filtered, ¼ the weight of 93 per cent. alcohol added, and the acids precipitated with hydrochloric acid; the precipitate, which consists of oxydigitogenic acid mixed with some digitic acid, is filtered off rapidly; the filtrate after a time deposits most of the digitic acid in aggregates of beautiful needles. If, however, a separation of the two acids is not obtained in this way, they are dissolved in potash, the solution diluted until it contains 1 per cent. of acid, and fractionally precipitated with hydrochloric acid, when oxydigitogenic acid is precipitated first. A separation by fractional crystallisation from alcohol and acetic acid is not possible, although the solubility of the two acids is very different. Digitic acid melts at 192°, dissolves easily in alcohol, chloroform, and acetic acid, and crystallises readily from boiling 50 per cent. alcohol, but not from strong alcohol. The *barium* salt, $(C_{10}H_{15}O_4)_2Ba + 6H_2O$, prepared by adding barium chloride to a solution of the potassium salt, crystallises in nodular aggregates, and is somewhat sparingly soluble in water. The *potassium* salt also crystallises well and is extremely soluble in water.

If the acid is dissolved in decinormal potash in the proportion, $C_{10}H_{16}O_4 : 1KOH$, and phenolphthaleïn and a few drops of alkali are added, the red colour remains both when the solution is allowed to stand and when heated : hence the acid is not a lactone.

The author reserves the theoretical consideration of the results for a future communication. E. C. R.

Hydrocotoïn, a Constituent of Coto-Bark. By G. Ciamician and P. Silber (*Ber.*, **24**, 299—301).—The molecular weight of hydrocotoïn (compare Jobst and Hesse, Abstr., 1880, 325) was determined by Raoult's method, with results which agreed well with those required by a compound of the molecular formula $C_{15}H_{14}O_4$. Quantitative experiments, carried out as described by Zeisel, showed that hydrocotoïn contains two methoxy-groups, $C_{13}H_8O_2(OMe)_2$

Methylhydrocotoïn, $C_{13}H_7O(OMe)_3$, is formed when hydrocotoïn is heated at 100° with methyl iodide and a solution of potash in methyl alcohol; it separates from alcohol in small, colourless needles, melts at 113°, and is readily soluble in ether and hot alcohol, but insoluble in water and alkalis.

When hydrocotoïn is heated with alcoholic potash in sealed tubes, it is decomposed, the products being probably a phenol-like substance and benzoic acid; its constitution may possibly be represented by the formula $COPh{\cdot}C_6H_2(OMe)_2{\cdot}OH$. F. S. K.

Cochineal-Carmine. By F. Lafar (*J. pr. Chem.* [2], **43**, 130—133; compare Abstr., 1885, 1076).—The sample of which the following is an analysis was purchased as "Carminnakarat"; it was a fine, loose powder, of full tone and warmth, and dissolved completely in ammonia. Liebermann's method of analysis (Abstr., 1885, 1076) was followed. The sample contained 0·4 per cent. of sulphur and 3·49 per cent. of nitrogen; its proximate percentage composition was:—

H_2O lost at 110°.	Ash.	Nitrogenous matter.	Colouring matter (by difference).
15·50	6·87	23·26	54·37

The percentage composition of the ash (8·14 per cent. of the dried colour) was:—

CuO.	SnO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.
0·35	0·14	40·48	44·20	0·61	5·40	3·20

P_2O_5.	SiO_2.	Fe_2O_3.	CO_2 (by difference).
2·71	0·60	trace	2·31

The molecular ratio of $Al_2O_3 : (CaO + MgO)$ is 1 : 2·044; Liebermann found it to be 1 : 1·972. A. G. B.

Synthetical Pyridine Bases of the β-Series. By C. Stoehr (*J. pr. Chem.* [2], **43**, 153—156; compare this vol., p. 219).—The β-methylpyridine obtained from glycerol (this vol., p. 219) contains pyridine and β-ethylpyridine. By fractionating the crude mixture of bases, about 10 per cent. of pyridine first distils over (b. p. 115°; m. p. of mercurochloride 177—178°), the β-methylpyridine being contained in the fraction 140—146°, from which it is obtained pure by conversion into the mercurochloride; it boils at 144—145° (corr.), and its sp. gr. at 0°/4° is 0·9751, that of the β-methylpyridine from strychnine being 0·9756. The melting point (201—202°) of the platinochloride cannot be made to agree with that given by Ladenberg (compare *loc. cit.*), but this salt forms asymmetric crystals, the investigation of which leaves no doubt as to their identity with the product obtained by Groth and Hjortdahl. The identity of the synthetical β-methylpyridine with that obtained from strychnine (this vol., p. 86) is thus established. The β-ethylpyridine was also isolated by means of its mercurochloride; it melts at 165° (corr.), and its sp. gr. at 0°/4° is 0·9585, that of the β-ethylpyridine obtained from brucine (this vol., p. 87) being 0·9590; the two bases are thus identical. β-Ethylpyridine is only slightly soluble in cold water, and practically insoluble in hot water; it has a stronger smell than the lower homologues; by oxidation with permanganate, it yields nicotinic acid (m. p. 230—231°). The *platinochloride* melts with decomposition at 208°; the *mercurochloride* forms short prisms which melt without decomposition at 131—132°. The *aurochloride* and the *picrate* were obtained. A. G. B.

Tinctorial Properties of Nitrosoxyquinolines. By S. v. Kostanecki (*Ber.*, **24**, 150—156).—3 : 4-Nitrosoparoxyquinoline has decided tinctorial powers, giving a green colour with iron mordants, and a brick-red with cobalt mordants, thus showing an analogy to 1 : 2-nitrosonaphthol. By the action of nitrous acid on orthoxyquinoline, two nitroso-derivatives are formed; the first, 1 : 4-nitrosoparoxyquinoline, is already known, and has no tinctorial properties; the second compound is much more readily soluble in water, and yields green and brownish-red "lakes" with iron and cobalt salts respectively. Amidorthohydroxyquinoline may be obtained from the corresponding nitroso-compound by reduction with stannous chloride; the sulphate crystallises with 2 mols. H_2O.

1 : 4-Nitrorthohydroxyquinoline, $OH{\cdot}C_9NH_5{\cdot}NO_2$, is prepared by the action of nitric acid on the nitroso-derivative; it crystallises from alcohol in small, yellow needles, melts at 173°, and is identical with the substance obtained from nitrorthoxyquinolinecarboxylic acid. The compound dyes green with iron mordants, and yellow with aluminium mordants. The corresponding nitroparhydroxyquinoline has no tinctorial properties.

Dinitrorthohydroxyquinoline,

$$C_9NH_4(NO_2)_2\ [OH : (NO_2)_2 = 1 : 2 : 4],$$

obtained by boiling the nitroso-derivative with nitric acid, is already known, and has only feeble tinctorial properties. J. B. T.

Quinolinedihydroximes. By S. v. Kostanecki and M. Reicher (*Ber.*, **24**, 156—159).—1 : 4-*Quinolinedioxime*, $C_9NH_5(NOH)_2$, is prepared by the action of hydroxylamine hydrochloride on nitrosorthoxyquinoline, and is deposited from dilute alcohol in small crystals which gradually decompose at 200°. It is soluble in soda and in sodium carbonate with a pale-yellow colour; it yields a stable, intense green "lake" with iron salts, but with cobalt salts inferior brown shades are formed. The *diacetate*, $C_9NH_5(NOAc)_2$, crystallises from glacial acetic acid, on the addition of water, in white needles which melt at 160° with decomposition.

A corresponding *dioxime* may be obtained from nitrosoparoxyquinoline by the action of hydroxylamine; it crystallises from alcohol in small needles and decomposes at 190°. A brown colour is formed with normal iron salts, but the tinctorial properties of the compound are only feeble. On boiling with dilute alkalis or with acetic anhydride, *quinoline dioxime anhydride*, $C_9NH_5{<}\genfrac{}{}{0pt}{}{N}{N}{>}O$, is formed; this crystallises from dilute alcohol in long, strongly refractive needles, melts at 134°, and is readily volatile with steam.

J. B. T.

Substitution Products of Isoquinoline. By A. Edinger and E. Bossung (*J. pr. Chem.* [2], **43**, 190—200).—*Isoquinoline dibromide*, $C_9NH_7Br_2$, is obtained by slowly dropping a solution of the calculated quantity of bromine in ether or chloroform into the same solvent containing isoquinoline suspended in it; the yellowish substance thus precipitated melts at 82° (uncorr.). The *hydrobromide*, $C_9NH_7Br_2,HBr$, is prepared by dissolving isoquinoline in an excess of aqueous hydrogen bromide and evaporating; it forms red crystals, which are unstable and melt between 130° and 135°.

Bromisoquinoline, C_9NH_6Br, is obtained by heating either of the preceding salts in an oil-bath at 180—200°, adding sodium hydroxide solution, and distilling with steam; the distillate is mixed with nitric acid and evaporated until the *bromisoquinoline nitrate* crystallises; the aqueous solution of this salt is then decomposed with ammonia, when the base separates as a thick, colourless oil which gradually crystallises; it melts at 40°, and boils at 280—285°. The *platinochloride* crystallises with 2 mols. H_2O; the *methiodide* melts at 233°; the *methochloride* melts at 82°, and yields an anhydrous *platinochloride*. *Bromisoquinoline benzyl chloride* is prepared by heating the base with benzyl chloride for two hours in a tube at 140°; it melts at 115°; its *platinochloride* is anhydrous. That the bromine atom is in the pyridine ring is evident from the fact that when bromisoquinoline is oxidised with potassium permanganate in alkaline solution, it yields a *bromopyridinedicarboxylic acid* which melts at 237°; its *barium salt* was obtained.

Nitrobromisoquinoline is obtained by dissolving bromisoquinoline (10 grams) in nitric acid of sp. gr. 1·52 (50 grams) and adding sulphuric acid of sp. gr. 1·84 (50 grams) while stirring and cooling. The mixture is allowed to stand until a portion of it gives no odour of isoquinoline when warmed with soda, and is then poured into water; the yellow flocks which separate are washed, dissolved in alcohol, and the solution decolorised with animal charcoal. It crystallises in white needles which melt at 173° (uncorr.), and dissolve sparingly in cold alcohol; when strongly heated, it sublimes in yellow leaflets, otherwise, in white needles. The *platinochloride* crystallises in tables; the *methiodide* forms reddish-yellow needles, and melts at 262°; the *methochloride* is more soluble than the methiodide, and crystallises in yellow needles which melt at 183°; its *platinochloride* was obtained.

On adding ammonia to the aqueous liquid from which the yellow flocks have separated (see above), a second *nitrobromisoquinoline* is obtained in white flocks; after crystallisation from alcohol, it melts at 158°, and dissolves in hot water, alcohol, and glacial acetic acid. Bromisoquinoline cannot be converted into a nitro-derivative by nitric acid alone, even when heated with it.

Amidobromisoquinoline is obtained from the nitro-compound melting at 173° by treating it with hydrochloric acid and stannous chloride in alcohol, and may be purified by sublimation; it melts at 136°, and dissolves in hot water, ether, chloroform, alcohol, and glacial acetic acid, and with a red colour in mineral acids; its *platinochloride* is described; its *methiodide* crystallises in red needles, and melts at 243°.

Dibromisoquinoline is prepared by diazotising the amido-compound in the presence of cuprous bromide; 6 grams of amidobromisoquinoline are dissolved in 180 grams of water containing 6 grams of sulphuric acid, 14 c.c. of a freshly prepared 15 per cent. solution of sodium nitrite are added, and the mixture poured slowly into a boiling solution (2 litres) of cuprous bromide in aqueous hydrobromic acid; when the reaction is completed, the solution is mixed with sodium hydroxide, distilled with steam, and the white flocks which pass over are crystallised from alcohol. It melts at 138°, and dissolves fairly easily in hot water, alcohol, ether, glacial acetic acid, and mineral acids.

A. G. B.

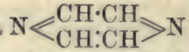
New Class of Organic Bases. By C. STOEHR (*J. pr. Chem* [2], 43, 156—160).—Besides the pyridine bases previously described (this vol., p. 579), the author has obtained by the action of ammonium salts on glycerol (this vol., p. 219) a new series of bases having the general formula $C_nH_{2n-4}N_2$; they are analogous in properties to the pyridine bases, and are isomeric with the aromatic diamines and hydrazines, the ketines, pyrimidines, and pyridazines; they may be regarded as homologues of the diamine $C_4H_4N_2$.

The only member of this series which has been properly investigated is $C_6H_8N_2$; it is a clear, strongly refractive liquid boiling at 153·5—154° (corr.) without decomposition. It has all the properties of a pyridine base, but is equally soluble in hot and cold water; it becomes hot on the addition of water; it is volatile in steam, and is precipitated from its aqueous solution by potash; its odour is very similar to that of the pyridine bases of higher molecular weight, and resembles that of nicotine. Its sp. gr. at 0°/4° is 1·0079. The *hydrochloride* is very soluble and hygroscopic; it sublimes on the water-bath. The *aurochloride*, $C_6H_8N_2,HAuCl_4,\frac{1}{2}H_2O$, crystallises in brilliant, lustrous, long, broad, brittle needles, which are sparingly soluble in cold water. The *platinochloride*,

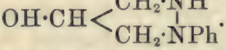
$$C_6H_8N_2,H_2PtCl_6 + 3H_2O,$$

forms lustrous crystals of the colour of potassium dichromate, and is freely soluble in water; when heated in aqueous solution, a heavy, yellow, crystalline powder, consisting of the *salt* $(C_6H_8N_2)_2,PtCl_4$, is deposited, and from the filtrate from this the *salt* $(C_6H_8N_2)_2,HCl,PtCl_4$ separates in lustrous, golden-yellow crystals. The *mercurochloride* forms brilliant, rhombohedral crystals, and is sparingly soluble. With methyl iodide, a crystalline *ammonium iodide* was obtained. When oxidised with permanganate, the base yields a sparingly soluble, nitrogenous acid, which melts at 250—251° with blackening; the silver and copper salts are sparingly soluble, and in aqueous solution the acid gives a red coloration with ferrous sulphate, which is permanent when heated.

The base, $C_8H_{12}N_2$ was also isolated; it boils at 178·5° (corr.); its sp. gr. at 0°/4° is 0·9852; it is volatile with steam and miscible with water. The *platinochloride*, *aurochloride*, and *mercurochloride* were obtained.

The author suggests the formula  $N\!<\!\genfrac{}{}{0pt}{}{CH{\cdot}CH}{CH{:}CH}\!>\!N$ for $C_4H_4N_2$; this, however, is identical with the formula for the ketine derivatives.

A. G. B.

New Base, $C_9H_{12}N_2O$, from Epichlorhydrin and Phenylhydrazine. By F. GERHARD (*Ber.*, **24**, 352—357).—By boiling epichlorhydrin with twice its weight of phenylhydrazine, Balbiano obtained as final products a mixture of aniline and phenylhydrazine, and explains the reaction by supposing that the phenylhydrazine first forms the additive compound $C_9H_{12}N_2O$, which then reacts with the phenylhydrazine hydrochloride, $C_9H_{12}N_2O + PhNH{\cdot}NH_2HCl = PhNH_2 + NH_4Cl + H_2O + C_3H_3N_2Ph$. The author has prepared this intermediate compound, and from its behaviour concludes that it has the constitution  $OH{\cdot}CH\!<\!\genfrac{}{}{0pt}{}{CH_2{\cdot}NH}{CH_2{\cdot}NPh}$. It is prepared as follows:—Epichlorhydrin (1 part) and phenylhydrazine (1·5 parts) are allowed to remain in ethereal solution. At a temperature below 15°, phenylhydrazine hydrochloride is slowly precipitated, the reaction being ended in about 14 days. On evaporating the filtered ethereal solution, a crystalline mass is obtained, which is purified by crystallisation from ether and carbon bisulphide, and finally from benzene. The new base crystallises from ether in hard, nacreous prisms, melts at 103—104°, is easily soluble in warm water, ether, alcohol, chloroform, and hot carbon bisulphide, and slowly turns yellow on exposure to light. By boiling with phenylhydrazine hydrochloride in benzene solution on the oil-bath, decomposition easily takes place, and the products are the same as those obtained by

Balbiano, namely, aniline and phenylpyrazole (the latter gave a platinum salt melting at 173°). The *platinochloride*,

$$(C_9H_{12}N_2O)_2,H_2PtCl_6,2H_2O,$$

obtained by adding a concentrated hydrochloric acid solution of platinic chloride, crystallises in beautiful, yellowish-red prismatic crystals, melts at 156° with decomposition, and is easily soluble in warm water and dilute alcohol, insoluble in ether.

The new base is easily acted on by oxidising agents. Nitric acid gives a violet coloration, which turns brown with excess of acid, or if left for a time. Chromic acid gives a bright red coloration. Potassium permanganate is reduced. With ferric chloride and hydrochloric acid, it gives a beautiful wine-red coloration. On reduction with sodium and absolute alcohol, phenylhydrazine is formed. The *acetyl* compound, $N_2PhH\cdot C_3H_5OAc$, is formed by boiling the base with acetic anhydride.
E. C. R.

Constitution of Nicotine. By F. BLAU (*Ber.*, **24**, 326—329).—The author has prepared α-β-dipiperidyl and compared it with hexahydronicotine obtained from nicotine by Liebrecht (Abstr., 1886, 161): he finds that these two compounds are not identical.

α-β-Dipyridyl was prepared from metaphenylenediamine by converting it into phenanthroline and dipyridyldicarboxylic acid. The corrected boiling point of the substance is 295·5—296·5°.

α-β-Dipiperidyl is obtained from the above compound by reducing it first with sodium and alcohol, as described by Ladenburg, then with sodium and amyl alcohol, as described by Bamberger. It distils at 268—270°, and the distillate solidifies to a crystalline mass which melts at about 30°; but on account of the hygroscopic nature of the substance the melting point is only approximate. The *hydrochloride* is easily soluble in water, very sparingly so in alcohol. The *platinochloride* is easily soluble in water, but not hygroscopic, and somewhat sparingly soluble in alcohol. The *aurochloride* is not so soluble in water, crystallises well, melts at 202°, and decomposes at 210°. Liebrecht's so-called dipiperidyl from nicotine is liquid, and yields an aurochloride melting at 131—132°. α-β-Dipiperidyl yields a well crystallised compound with carbon bisulphide, and also a nitroso-compound.

From a consideration of the boiling points of the dipiperidyls at present known, the author is inclined to think Liebrecht's hexahydronicotine does not belong to the dipiperidyl series. He is at present engaged in the preparation of ββ-dipiperidyl, and the examination of the behaviour of hexahydronicotine on further reduction.
E. C. R.

Isocinchonine. By O. HESSE (*Annalen*, **260**, 213—226; compare Comstock and Koenigs, Abstr., 1887, 1124).—Isocinchonine, $C_{19}H_{22}N_2O$, is formed when commercial cinchonine sulphate (30 grams) or the free base is dissolved in concentrated sulphuric acid (150 grams), the solution heated at 60—80° for six hours, and then kept for 24 hours at the ordinary temperature; the solution is diluted, gradually mixed with excess of soda, and extracted with ether; on concentrating the ethereal extract, small quantities of hydrocinchonine and apocinchonine are deposited in crystals, and on further evaporation, there remains an oily residue which gradually solidifies, and from which pure isocinchonine can be obtained by repeated recrystallisation from ether, or by converting the base into the hydrochloride. Isocinchonine crystallises from ether in compact, colourless, anhydrous prisms, melts at 125°, volatilises at a high temperature, and is moderately easily volatile with steam; it is readily soluble in alcohol, ether, acetone, chloroform, and light petroleum, but insoluble in water and alkalis. Its alcoholic solution turns red litmus blue, but has no action on phenolphthaleïn paper; an absolute alcoholic solution of the base is lævorotatory, and at 15° $[\alpha]_D = -53\cdot7°$ when $p = 1$, and $[\alpha]_D = -55\cdot6°$ when $p = 3$. The *hydrochloride*, $C_{19}H_{22}N_2O,HCl + H_2O$, prepared by neutralising the base with dilute hydrochloric acid, crystallises in hexagonal prisms, and loses its water at 140—150°, the anhydrous salt melting at 201°; it is readily soluble in hot water, and moderately easily in alcohol and chloroform, but only sparingly in cold water, and insoluble in ether; its rotatory power at 15° in aqueous solution is $[\alpha]_D = -68\cdot6$ when $p = 1$, and $[\alpha]_D = -71\cdot2°$ when $p = 2$, but the addition of hydrochloric acid to the solution diminishes the rotatory power. The *platinochloride*, $(C_{19}H_{22}N_2O)_2,H_2PtCl_6 + 3H_2O$, prepared by adding sodium platinochloride to an aqueous solution of the hydrochloride, is a pale yellow, sparingly soluble compound. The *acid platinochloride*, $C_{19}H_{22}N_2O,H_2PtCl_6 + 2H_2O$, is precipitated on adding platinic chloride to an aqueous solution of the hydrochloride, but the yellow, amorphous compound thus produced readily loses 1 mol. H_2O, changing into a crystalline salt; the latter forms orange needles, and is rather sparingly soluble in hydrochloric acid, and almost insoluble in cold water. The *aurochloride*, $C_{19}H_{22}N_2O,2HAuCl_4$, is obtained as a yellow, amorphous precipitate on adding auric chloride to an aqueous solution of the hydrochloride; it is sparingly soluble in cold water. The *mercurochloride*, $C_{19}H_{22}N_2O,HHgCl_3$, crystallises in small, concentrically grouped needles. The *normal sulphate*, $(C_{19}H_{22}N_2O)_2,H_2SO_4 + 6H_2O$, crystallises in prisms, and is readily soluble in alcohol and water; the *acid sulphate*, $C_{19}H_{22}N_2O,H_2SO_4 + 4H_2O$, crystallises in needles, and is readily soluble in hot, but only moderately easily in cold, water. The *oxalate*, $(C_{19}H_{22}N_2O)_2,H_2C_2O_4$, *thiocyanate*, *hydriodide* (with 1 mol. H_2O), and the zinc double salt, $C_{19}H_{22}N_2O,2HCl,ZnCl_2$, crystallise in needles.

When "pure" commercial cinchonine acid sulphate is boiled with dilute sulphuric acid as described by Jungfleisch and Léger (Abstr., 1888, 380), small quantities of apocinchonine and cinchonigine are formed, but cinchonibine and the two hydroxy-bases described by Jungfleisch and Léger are not produced; cinchonifine and cinchoniline are probably identical with hydrocinchonine and apocinchonine respectively, and cinchonigine is identical with isocinchonine.

When cinchonine sulphate is treated with sulphuric acid and oxalic acid at 125—130°, as described by Caventou and Girard, it yields hydrocinchonine, isocinchonine, and a base which is probably identical with that formed by heating cinchonicine oxalate with sulphuric acid; it would seem, therefore, that in this reaction some of the cinchonine is converted into cinchonicine. F. S. K.

Veratrine. By S. STRANSKY (*Monatsh.*, **11**, 482—485).—The alkaloïd dissolves readily in most solvents, such as xylene, glycerol, aniline, acetone, chloroform, and amyl alcohol. On distillation with alcoholic potash, commercial veratrine gave rise to the two bases cevidine and veratroïne; angelic and veratric acids were simultaneously formed, and the latter identified both by its melting point (179·5°) and by a combustion. When distilled with aqueous potash, the yellow, resinous mixture of bases furnished methylamine, recognised by its forming the characteristic platinochloride, and a yellow oil having an odour resembling that of the homologues of pyridine. The author has also investigated the behaviour of veratrine when distilled with zinc dust and when oxidised with potassium permanganate. In the former case, no recognisable product was obtained; in the latter traces of oxalic acid were formed (compare Bosetti, *Arch. Pharm.*, 1883, 81, and Ahrens, Abstr., 1890, 1448).

G. T. M.

A Double Salt of Cocaïne. By W. MÜLLER (*Chem. Centr.*, 1890, ii, 818; from *Pharm. Zeit.*, **35**, 522).—On adding cocaïne hydrochloride to a solution of mercuric chloride (1 : 50), a milkiness soon forms which gradually increases to a voluminous precipitate. It is the double salt $C_{17}H_{21}NO_4,HCl,HgCl_2 + 2H_2O$, sparingly soluble in cold water, somewhat more soluble in alcohol; it forms slender crystals, and melts at 124°. If heated with hydrochloric acid in the absence of air, benzoic acid, methyl benzoate, and ecgonine hydrochloride are formed. After agitating the aqueous solution with chloroform, cocaïne can be detected in the former with picric acid. Alcoholic potash decomposes the double salt, mercuric oxide being precipitated and ethyl benzoate formed. J. W. L.

Cocaïne Chromate. By W. MÜLLER (*Chem. Centr.*, 1890, ii, 818—819; from *Pharm. Zeit.*, **35**, 594).—If a concentrated solution of cocaïne is treated with a 4—5 per cent. solution of chromic acid, a precipitate is gradually formed of a thick, tarry nature, which finally changes to a light-yellow, amorphous precipitate of the composition $C_{17}H_{21}NO_4,H_2CrO_4 + H_2O$. In the presence of free hydrochloric acid, the chromate is precipitated almost quantitatively, and is of a lemon-yellow colour; 0·001 gram is precipitable. It is not hygroscopic, is sparingly soluble in cold water, but readily so in hot water, from which it crystallises in orange-coloured needles which darken on exposure to the light.

The precipitation in acid solution may serve to distinguish cocaïne from other alkaloïds. Potassium dichromate precipitates the same double salt in neutral solution; but normal potassium chromate produces no precipitate in the neutral solution; on the addition of acid, the double salt is formed. It melts at 127°. By treating it with fuming nitric acid, drying, and then adding alcoholic potash, the odour of peppermint is perceptible, which De Silva considers as characteristic of cocaïne. If the chromate is warmed with alcoholic potash, the odour of ethyl benzoate is perceptible. The chromate is insoluble in benzene, and but slightly soluble in chloroform.

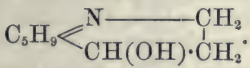
J. W. L.

Oxidation of Hygrine. By C. LIEBERMANN and O. KÜHLING (*Ber.*, **24**, 407—415).—Liebermann has already shown (Abstr., 1889, 732) that the hygrine obtained from coca or truxillo leaves is a mixture of liquid bases which are very difficult to separate. He succeeded in isolating two constituents, and termed them "low-boiling hygrine," $C_8H_{15}NO$, and "high-boiling hygrine," $C_{14}H_{24}N_2O$. A crude hygrine, from which the same compounds may be separated, has been obtained in larger quantity from Peruvian cusco leaves. The low-boiling hygrine yields a *hydrochloride*, $C_8H_{15}NO,HCl$, crystallising in beautiful needles if moisture be excluded, and a *hydriodide*, $C_8H_{15}NO,HI$, of similar appearance; the high-boiling hygrine forms a *hydrobromide*, $C_{14}H_{24}N_2O,2HBr$, and a *hydriodide*, $C_{14}H_{24}N_2O,2HI$, also crystallising in colourless needles.

Many unsuccessful attempts were made to obtain crystallised products by the oxidation of hygrine; at length it was found that the following method yielded good results:—40 grams of hygrine is mixed with a solution of 100 grams of chromic anhydride, and 150 grams of concentrated sulphuric acid in about 600 grams of water, and the mixture boiled for 4—5 hours. After removal of chromium and sulphuric acid, the solution is boiled with baryta-water, treated with carbonic anhydride, and the remainder of the barium exactly precipitated with sulphuric acid. The filtrate is evaporated to a small bulk, and treated with freshly precipitated copper oxide; the copper salt thus formed, when purified, crystallises in pale-blue needles, readily soluble in water and alcohol, and has the composition $(C_6H_{10}NO_2)_2Cu$. It is readily converted into the corresponding acid, which may be termed *hygric acid*, $C_6H_{11}NO_2$. This forms colourless, stellate groups of needles, is readily soluble in water, alcohol, and hot chloroform, insoluble in ether and benzene, and is somewhat hygroscopic if not quite pure; after drying at 60°, it melts at 164°, but under ordinary circumstances, becomes plastic at 85°, and finally melts completely at 130°. This behaviour may possibly be due to the absorption of water from the atmosphere. It decomposes if strongly heated, evolving vapours which smell like pyridine; it reduces potassium permanganate in the cold. Its *hydrochloride*, $C_6H_{11}NO_2,HCl$, crystallises in beautiful needles, and melts at 188°; the *aurochloride*, $C_6H_{11}NO_2,HAuCl_4$, is an oil.

Attempts were also made to prepare the calcium and barium salts, but without success, owing, probably, to the fact that the compound is the carboxylic acid of a strong base, and the acid nature of the compound is so much weakened that its salts with those metals are very unstable. The composition and general properties of the acid make it not improbable that it is a piperidinecarboxylic acid, $C_5NH_{10}\cdot COOH$. When quickly heated to 300° with concentrated sulphuric acid, it yields a mixture of pyridine and piperidine; if also the acid is boiled with an excess of auric chloride, gold is precipitated, and a mixture of pyridine and piperidine aurochlorides is obtained.

From these results, as well as from the composition of the alkaloïd, the latter cannot be a trimethylquinoline, as suggested by Hesse (*Pharm. Zeit.*, 1887, 669). It is more probably a hydroxy-allylpiperidine, $C_5NH_{10}\cdot OC_3H_5$, or has possibly the constitution



$$C_5H_9 < \begin{matrix} N\text{———}CH_2 \\ CH(OH)\cdot CH_2 \end{matrix}.$$

The high-boiling hygrine, on oxidation, also yields hygric acid, although in much smaller quantity, and is therefore likewise closely connected with piperidine. H. G. C.

Cytisine. By K. Buchka and A. Magalhães (*Ber.*, **24**, 253—260).—Cytisine may be prepared by the following method more readily than by Partheil's process (this vol., p. 231):—the ground laburnum seeds are extracted with dilute hydrochloric acid, and the solution, after concentration, is made alkaline and extracted with chloroform. On distilling off the latter, cytisine remains as a pale-yellow oil which quickly solidifies to a crystalline mass, and may be obtained almost colourless by repeated crystallisation from absolute alcohol. It forms transparent, envelope-shaped crystals, melts at 156° (uncorr.), and may be sublimed; it is very readily soluble in water, alcohol, benzene, and chloroform, but insoluble in carbon bisulphide and light petroleum. Analysis and determination of the molecular weight by Raoult's method have confirmed the formula $C_{11}H_{14}N_2O$, first given by Partheil. It yields two *hydrochlorides*, the first of which, $C_{11}H_{14}N_2O,HCl$, is obtained by passing hydrogen chloride into a chloroform solution of the base; the dried salt is an amorphous powder, but it crystallises from alcohol in colourless, monosymmetric prisms ($a : b : c = 0{\cdot}731 : 1 : 0{\cdot}714$; $\beta = 107{\cdot}5°$), containing $\frac{1}{2}$ mol. alcohol. The *dihydrochloride*, $C_{11}H_{14}N_2O,2HCl + 2\frac{1}{2}H_2O$, is obtained by acting on the base with an excess of hydrochloric acid, and crystallises from water in small, hard, colourless crystals. The base also forms two *platinochlorides*, $(C_{11}H_{14}N_2O)_2,H_2PtCl_6 + 2H_2O$ and $C_{11}H_{14}N_2O,H_2PtCl_6 + 2\frac{1}{2}H_2O$. The latter has already been described by Partheil; the former crystallises in pale-yellow, lustrous needles or plates, is sparingly soluble in water, and decomposes on heating without melting. The *aurochloride* has also been described by Partheil; the *zincochloride*, $C_{11}H_{14}N_2O,H_2ZnCl_4$, forms small, colourless, transparent crystals very readily soluble in water.

On distillation with soda-lime, cytisine yields a distillate which smells strongly of pyrroline, and of pyridine and quinoline bases. Pyrroline is also formed by heating cytisine alone or with zinc-dust. Potassium permanganate converts the base into a syrupy acid insoluble in ether. H. G. C.

Crystals Occurring in the Nuclei of the Liver Cells. By V. Grandis (*Rend. Acad. Lincei.*, **6**, ii, 213—218 and 230—235).—The author has previously described (*Atti. Acad. Real. Torino*, March, 1889) certain crystals found exclusively in the cell nuclei of the liver and some other organs of adult and old dogs. On account of the interference of the enveloping nuclear matter, the reactions given by the crystals *in situ* under the microscope were untrustworthy, but the author has now succeeded in separating them, and has extracted from them a new alkaloïd or ptomaïne which he terms *gerontine.* Gerontine is a strongly basic compound isomeric with cadaverine; it is a heavy, yellowish liquid which resinifies on standing. It has a disgusting odour, dissolves in water, and gradually crystallises out from its solution in spherical tufts; when heated with caustic potash, an alkaline gas is evolved. The *hydrochloride* crystallises from absolute alcohol in very deliquescent, rectangular, and oblique prisms. The *platinochoride*, $C_5H_{14}N_2,H_2PtCl_6$, crystallises in tufts of pale-yellow, spindle-shaped needles readily soluble in water, but insoluble in alcohol. It blackens and decomposes at 215°. The *aurochloride* crystallises in yellow needles very soluble in alcohol and water. A compound of the hydrochloride with mercuric chloride, $C_5H_4N_2,2HCl,HgCl_2 + 2H_2O$, may also be obtained; it crystallises in deliquescent, rectangular prisms and cubes, and decomposes when heated above 100°. The *picrate* forms very soluble, yellow, twinned, lenticular crystals. A *benzoyl* derivative crystallises in rectangular prisms which melt at 175—176°. With phosphotungstic acid, gerontine yields a white, granular precipitate which crystallises, on cooling, in rectangular prisms; with phosphomolybdic acid, a precipitate of yellow, hexagonal crystals is obtained, which turn first green and then blue; potassium bismutho-iodide yields a precipitate of red prisms; with potassium iodide, an amorphous, yellow precipitate; with tannic acid, a white, amorphous precipitate which turns brown after a time; with Fröhde's reagent, a transient, red coloration is obtained. From various considerations, the author concludes that the nuclear crystals consist of gerontine phosphate. S. B. A. A.

Synthesis of Proteïds. By P. SCHÜTZENBERGER (*Compt. rend.*, **112**, 198—201).—The author's previous researches on the decomposition of albumin in presence of alkalis (Abstr., 1888, 971) lead to the conclusion that albumin may be broadly regarded as formed from $H_2C_2O_4 + 2NH_3 + 3C_mH_{2m+1}NO_2 + 3C_nH_{2n-1}NO_2$ with elimination of 8 mols. H_2O. This would give $C_{q+2}H_{2q-8}N_8O_8$, and if $q = 28$, the percentage composition calculated from the formula agrees closely with that of albumin.

Amido-compounds, $C_mH_{2m+1}NO_2$ and $C_nH_{2n-1}NO_2$, mixed with about 10 per cent. of urea, were finely powdered, dried at 110°, and intimately mixed with 1·5 times the weight of phosphoric anhydride, and heated in an oil-bath. At 120°, there is no change, but at 125°, dehydration takes place very rapidly, and the mixture becomes pasty, but solidifies to a compact product without any appreciable darkening. The product is dissolved in water, the solution mixed with several times its volume of alcohol, and the pasty precipitate washed with alcohol and redissolved in water. Phosphoric acid is removed by means of baryta, and the filtered liquid, when concentrated on a water-bath, yields an amorphous product, soluble in water, but precipitated as a curdy mass on the addition of alcohol. Aqueous solutions of the product are precipitated by tannin, picric acid, mercuric chloride, acid mercuric nitrate, Millon's reagent, potassium diiodide, mercuric potassium iodide, phosphotungstic acid in presence of hydrochloric acid, phosphomolybdic acid, and lead acetate and basic acetate. Potassium ferrocyanide gives no precipitate in a cold solution in presence of acetic acid. With caustic potash and copper sulphate, a rose-red coloration is formed. Heated with nitric acid and evaporated with excess of the acid, the product yields a yellow residue which becomes orange in contact with ammonia, and when heated decomposes suddenly, leaving a bulky mass of carbon. Its behaviour in this respect is similar to that of gelatin. When heated on platinum, the compound carbonises and swells up, evolving the characteristic odour of burning nitrogenous animal matter.

C. H. B.

Action of Glycerol on Egg Albumin. By V. GRANDIS (*Rend. Acad. Lincei*, **6**, ii, 138—145).—Berthelot found that when glycerol is left in contact with albumin, it is converted into sugar, and suggested that, in virtue of this reaction, sugar might be formed from the animal fat. The author has examined the change produced by the reaction in the albumin. Purified egg albumin was boiled with an equal volume of pure glycerol (sp. gr. = 1·25) for one-half to one hour, filtered, and the filtrate extracted with at least 10 vols. of alcohol (90°) containing a little ether. The extract is a milky liquid which in a day or two leaves a white, flocculent deposit; this dissolves in boiling water, forming a heavy, opalescent solution not coagulated by boiling, and unaffected by the addition of acetic or hydrochloric acids, or of a concentrated solution of sodium chloride. The addition of a concentrated solution of sodium sulphate or chloride, together with a drop of acetic acid, produces a flocculent precipitate soluble in the boiling liquid. Concentrated nitric acid gives a precipitate which dissolves on heating, forming a pale-yellow solution, which acquires a reddish-violet coloration on the addition of soda and a drop of copper sulphate. It is also precipitated by the other reagents for proteïds. In its reactions it strongly resembles hemialbumose, but it does not appear to have the same percentage composition, approximating in this respect to antipeptone. It is probably identical with the compound obtained by Hönig (*Chem. Zeit.*, 1890, Nos. 53 and 55), but if so, its alleged solubility in alcohol and ether must be due to the use of a quantity of the solvent insufficient to precipitate it from its solutions. It appears to be formed by the direct action of glycerol on albumin, since it may be obtained without the aid of heat by leaving the two substances in prolonged contact at the ordinary temperature. Assuming that the proteïd is hemialbumose, it is probable that as a first step to its conversion into sugar, the glycerol is dehydrated and converted into acraldehyde.

When an aqueous solution of the purified proteïd is treated with a quantity of alcohol insufficient to form a precipitate, and allowed to remain for about three months, a crystalline deposit of very thin, brilliant, rhomboidal, curved plates is formed. These crystals are insoluble in hot water, and in concentrated sulphuric acid and potash; they are turned yellow by iodine, but are not affected by Millon's reagent, and do not react with alloxan. S. B. A. A.

Decomposition Products of Proteïds. By M. SIEGFRIED (*Ber.*, **24**, 418—432).—It has been shown by Dreschsel (Abstr., 1889, 1021, this vol. p. 95) that two bases may be isolated by means of phosphomolybdic acid from the products of decomposition of caseïn with hydrochloric acid, and that one of them when heated with baryta-water yields carbamide. The author has extended the investigation to other proteïds, with the results given in this paper.

400 grams of conglutin is boiled with 1600 c.c. of 15 per cent. hydrochloric acid and 100 grams of stannous chloride for 72 hours, air being excluded, and the product after dilution to 7 litres, is saturated with hydrogen sulphide; the filtrate is evaporated, and a solution of 2500 grams of crystallised phosphomolybdic acid added, preferably to the hot solution, and the precipitate washed with a solution of phosphomolybdic acid in dilute sulphuric acid until free from chlorine.

The filtrate in addition to the decomposition products obtained by Ritthausen (this Journ., 1870, 719, 721) and Schulze (Abstr., 1885, 581, 916), namely, glutamic acid, tyrosine, leucine, aspartic acid, and phenylalanine, also contains a compound which remains after separation of the foregoing substances as a syrup. On the addition of an alcoholic solution of hydrogen platinochloride, it yields a platinochloride, which is reconverted by the action of hydrogen sulphide and hydrated lead oxide into the base. This separates as a granular precipitate on the addition of ether to its alcoholic solution; it has the empirical formula $C_4H_8NO_2$, and belongs to the class of glucoproteïns described by Schützenberger (Abstr., 1879, 542).

The precipitate obtained with phosphomolybdic acid is boiled with baryta-water, filtered, the barium exactly precipitated with sulphuric acid, again filtered, and, after the addition of an excess of hydrochloric acid, evaporated to a syrup. By repeated precipitation with alcohol, this can be separated into a more readily soluble and a less readily soluble portion. From both fractions, however, a *platinochloride*, $C_8H_{22}N_2O_3PtCl_6$, and a double salt with silver nitrate,

$$C_6H_{13}N_3O_2,HNO_3,AgNO_3,$$

were obtained; both salts have the same composition as those obtained by Dreschsel from caseïn. The former crystallises when pure in orange needles, but is frequently obtained as an oil. The second forms light, slender needles, but always contains small quantities of an amorphous silver salt.

These three salts may be more readily prepared in the following manner:—The precipitate obtained with phosphomolybdic acid is dissolved in hot water, decomposed with a slight excess of baryta-water, the filtrate saturated with carbonic anhydride, and heated for half an hour to boiling. Silver nitrate is then added directly to the solution until no further separation of the amorphous silver salt takes place. After remaining for 12 hours, the precipitate is separated, the filtrate evaporated to a syrup, and alcohol is added in small quantities; the silver salt of the base which yields the above platinochloride first separates as an oily precipitate, and is quite free from the salt $C_6H_{13}N_3O_2,HNO_3,AgNO_3$, which separates completely on further addition of alcohol and ether. The oily silver salt is then converted into the platinochloride, by decomposing it with hydrogen sulphide, evaporating to a small bulk, and adding hydrogen platinochloride, alcohol, and ether.

When phosphomolybdic acid is added to the product of the reaction of hydrochloric acid and 20 grams of glutenfibrin, hemiproteïn, oxyprotosulphonic acid, or egg-albumin, a precipitate is formed from which in all cases the above platinochloride and crystalline and amorphous silver salts may be obtained. The egg-albumin product contains other bases which have not as yet been isolated.

The amorphous silver salt, which appears to have the composition $C_{11}H_{17}N_6O_6Ag_3$, when decomposed by hydrogen sulphide and treated with hydrochloric acid, yields the compound $C_{11}H_{20}N_6O_6,2HCl$, crystallising in short prisms; the platinochloride, $C_8H_{22}N_2O_3PtCl_6$, was found to contain 1 mol. alcohol of crystallisation, and has therefore the composition $C_6H_{14}N_2O_2,H_2PtCl_6 + EtOH$. On treating it with hydrogen sulphide and adding hydrochloric acid, it yields the *hydrochloride*, $C_6H_{14}N_2O_2,2HCl$, crystallising in lustrous needles. The compound $C_6H_{14}N_2O_2,H_2PtCl_6 + MeOH$ has also been prepared.

When the platinochloride containing 1 mol. alcohol is freed from platinum and heated with baryta-water at 150°, a product is formed which yields a platinochloride containing no alcohol, namely, $C_6H_{14}N_2O_2,H_2PtCl_6$. If the corresponding hydrochloride is heated with alcohol and hydrogen platinochloride, it again, however, yields the original platinochloride. This is due to the fact that the base is converted by heating with baryta-water into an optical isomeride, for whereas the solution of the original base is strongly dextrorotatory, the solution, after heating, is practically inactive. This behaviour is analogous to that of the optically active amido-acids, observed by Schultze (*loc. cit.*). H. G. C.

Preservation of Oxyhæmoglobin. By L. FREDERICQ (*Trav. de Lab. de L. Fredericq, Liége*, **3**, 109).—Solutions of crystals of oxyhæmoglobin can be kept unchanged for months in contact with the air provided that the atmospheric micro-organisms be excluded by careful antiseptic precautions. In sealed tubes, the pigment changes to methæmoglobin after the lapse of some months; if, however, putrefaction occurs, reduced hæmoglobin makes its appearance (compare Yeo, Abstr., 1890, 1012). W. D. H.

Preservation of Hæmocyanin. By L. FREDERICQ (*Trav. de Lab. de L. Fredericq, Liége*, **3**, 194).—Hæmocyanin, when preserved in a closed vessel, even though putrefaction may occur, remains unaltered in its characteristic properties for at least six months.

W. D. H.

Electrolysis and Putrefaction of Bile. By G. N. STEWART (*Studies from Physiol. Lab., Owens College*, **1**, 201—206).—When ox bile putrefies, the pigment changes to brown and ultimately to yellow, and Gmelin's colour reaction is no longer given. Bile pigment slowly undergoes the same change even if putrefaction is prevented. When bile is electrolysed in a U-tube, changes take place at the negative pole similar to those just mentioned. In the earlier stages, reversal of the current restores the original colour. The anode has an oxidising, the cathode a reducing, action. During all these changes, however, the spectrum remains unaltered, except that the absorption bands become slightly less marked under anodic, more marked under cathodic, influence. Cholohæmatin, to which the bands of ox-bile are due, must, therefore, differ in stability from the bile pigments proper. The bile salts are electrolytes, and an acid constituent of these crystallises at the anode in long needles; but the conductivity of bile salts is small as compared with that of the inorganic constituents of the secretion (compare Haycraft and Scofield, Abstr., 1890, 181).

W. D. H.

Physiological Chemistry.

Respiratory Exchanges in Animals. By H. C. CHAPMAN and A. P. BRUBAKER (*Proc. Acad. Nat. Sci., Philadelphia*, 1891, 13—44). —A series of analyses relating to the consumption of oxygen and the production of carbonic anhydride were performed with a Regnault-Reiset apparatus, on a number of animals, chiefly rabbits. It was found that on the average the rabbit consumes 2·01 grams of oxygen per hour, and 0·8 gram of oxygen per hour per kilo. of body weight, and produces 2·5 grams of carbonic anhydride per hour, and 1·1 grams of carbonic anhydride per hour per kilo. of body weight; the respiratory quotient averaging 0·9. W. D. H.

Action of Organic Acids on Salivary Digestion. By O. JOHN (*Virchow's Archiv*, **122**, 271—283).—The addition of minute quantities of organic acids (formic, succinic, acetic, oxalic, malic, lactic, butyric, &c.) to saliva, and the influence of such additions on the activity of its amylolytic ferment, were carried out in artificial digestion experiments, and the conclusions arrived at are the following :—

(1.) In very small quantities, these acids act, as hydrochloric acid has been shown previously to act (Chittenden and Smith, Abstr., 1886, 638), favourably on the diastatic activity of saliva.

(2.) This action depends on the formation of a compound with the alkaline constituents of the saliva.

(3.) Very small quantities of free acid, however, retard the action of the ferment.

(4.) The coefficient of retardation stands in no relation to the chemical constitution of the acid. Oxalic acid, of the acids used, is the most powerful in this direction, and of the acids most commonly found in ordinary foods, acetic acid is the least powerful.

(5.) A comparison is drawn between the action of these acids on the salivary enzyme, and the similar action they have on bacterial activity. W. D. H.

Hydrochloric Acid in Gastric Juice. By E. Salkowski and M. Kumagawa (*Virchow's Archiv*, **122**, 235—252). G. Klemperer (*Zeit. Klin. Med.*, **14**) states that none of the chemical methods for the estimation of free hydrochloric acid in gastric juice takes into account the possibility that the acid may be united to organic bases, such as leucine and glycocine, basic products of the lactic acid fermentation, and quinine. A repetition of some of Klemperer's experiments with artificial mixtures containing such bases led to the following results. It was found that, although the acid might be united to bases of the amido-acid series, as for instance, to form leucine hydrochloride, it still remains physiologically active, that is to say, digestion occurs as well in a mixture containing leucine hydrochloride as in one containing an equivalent amount of free hydrochloric acid. For all practical physiological purposes, the hydrochloric acid is as free in such compounds as if it were actually or chemically free. Those methods like Cahn and v. Mering's cinchonine method, or Sjöquist's method (Abstr., 1889, 302), are therefore perfectly correct as a means of ascertaining the quantity of "physiologically free" hydrochloric acid. Among qualitative reactions, the methyl-violet test is in the same sense a trustworthy one; leucine hydrochloride gives, however, a slight violet tint to the blue colour produced. Günzburg's reaction, however, gives a negative result with these compounds.

Organic bases like quinine, when united with hydrochloric acid, form a compound which is neutral or weakly alkaline. Such a solution has, under no circumstances, any peptic activity; the acid is neither chemically nor physiologically free, and in this case Sjöquist's method of estimating the acid would lead to a false result. Hydrochloric acid which contains in solution half the amount of quinine necessary to saturate it, is physiologically inactive, although it is partly chemically free. Under such circumstances, Sjöquist's method is again inapplicable, and the qualitative reactions before mentioned are both untrustworthy.

Experiments such as these do not lead to the conclusion that these methods are not applicable to the investigation of human gastric juice. Until it is shown that human gastric juice contains organic bases which act like quinine, the methods at present in use must be regarded as perfectly trustworthy. W. D. H.

Absorption of Fats in the Absence of Bile. By I. Munk (*Virchow's Archiv*, **122**, 302—325).—The classical experiments of Bidder and Schmidt showed that, without bile, fat was very badly absorbed. Since then, investigations by Voit and by Röhmann (*Pflüger's Archiv*, **29**, 509) have confirmed this; Voit states that in dogs with a biliary fistula, in which no bile can, therefore, enter the intestine, the excess of fat found in the fæces is contained as such, and is only to a slight extent resolved into fatty acids and glycerol. Röhmann, however, who made accurate quantitative experiments on this point, states that before the operation one-fifth of the fatty substances contained in the fæces were present as neutral fats, and four-fifths as fatty acids and soaps; and after the operation these fractions were respectively one-eleventh and ten-elevenths.

Röhmann concludes that in dogs with biliary fistula, the chief mass of the fat is hydrolysed in the intestine by pancreatic juice and putrefactive bacteria, and the fatty acids so liberated are partly combined to form soaps.

Each of the experiments in the present research lasted three days; by feeding the animal (dog) on bone mixed with charcoal before and after the experiment, the fæces belonging to the time of the experiment would be easily recognised. The dog used had a biliary fistula, and was prevented from licking the bile from the external opening.

The following is a summary of the experiments performed:—

I. 3 grams of pork fat per kilo. of body weight *per diem*.

In the food,	1090 grams dry substance,	247·6 fat,	56·5 N.
In the fæces,	135·5 grams ,,	82·1 ,,	5·64 N.

60 per cent. of the dry fæces were fatty substances. The fatty substances were of the following nature:—

Neutral fat	7·85	grams.
Free fatty acids	61·84	,,
Fatty acids in soap	10·93	,,
Cholesterol	1·43	,,

Thus the amount of disintegrated fat was ten times as abundant as that of neutral fat.

II. 3 grams of fatty acids (from pork fat) per kilo. *per diem* mixed with a little horse fat. The fatty substances in the fæces were:—

Neutral fat	6·4	grams.
Free fatty acids	45·01	,,
Soaps	14·29	,,
Cholesterol	1·49	,,

Thus, of the total fatty material in the food (237·6 gram), 72·8 grams appeared in the fæces which contained 60 per cent. of their solid constituents as fatty substances. Comparing experiments I and II, the amount digested is rather greater in the latter than in the former.

	I.	II.
Percentage of dry material absorbed	87·6	89·7
,, fatty substances	66·9	72·8
,, nitrogen	90·0	92·4

In a dog without bile in his intestine, the absorption of fatty acids is thus better than that of neutral fats; in a normal dog, the substitution of an equivalent amount of fatty acid for fat causes no appreciable difference.

A similar series of experiments with mutton suet and an equivalent quantity of its fatty acids gave a similar result, except that this form of fat is not so well absorbed as pork fat. The percentage of fatty substances absorbed when given as fat was 35·5; when given as fatty acids, 42·2.

With larger doses of fat *per diem*, other series of experiments showed that the percentage absorbed was about the same, and that more was absorbed if fatty acids instead of neutral fats were given.

In the course of the research, it was noted that the colour of the fæces was pitch black when the diet given was meat free from fat. This cannot have been due to any derivative of the bile pigment, but to hæmatin (or some other derivative) of the hæmoglobin of the food. W. D. H.

Digestibility of Meadow Hay, Bean, Barley, Swedes, and Rice Meal. By F. Lehmann and J. H. Vogel (*Bied. Centr.*, **20**, 12—19; from *Journ. Landw.*, **38**, 165).—The experiments were made with two sheep, under similar conditions to the previous ones. The feeding during the six periods of the experiments was as follows:—Period No. 4, meadow hay. No. 1, hay and beans. Nos. 2, 5 and 6, hay and beans with swedes, rice meal, and barley respectively. No. 3, hay, beans, barley, and swedes. The amounts and composition of the foods and of the fæces of the six periods for each sheep are given in tables. The following table shows the average percentage amount of dry substance, and of the various constituents digested.

	Dry matter.	Crude proteïn.	Fat.	Ash.	Crude fibre.	Non-nitrogenous extract.
Hay	62·24	53·36	42·93	52·10	60·71	67·68
Beans	80·02	88·64	49·05	49·44	—	88·76
Swedes	96·28	62·26	93·46	52·60	100·0	99·05
Rice meal	66·02	44·45	83·15	10·09	34·37	83·84
Barley	90·80	63·17	77·84	11·55	100·0	96·16

The co-efficients for swedes are new. Those of hay and beans agree, on the whole, with the means in Wolff's tables. A slight error was made in the case of the crude fibre of beans. The negative result is explained by too high a coefficient having been found for hay. Barley and rice meal show greater differences from the numbers previously found. But the authors consider that, as regards barley, their numbers are nearer the truth than those obtained by Maercker and Schulze (*Journ. Landw.*, 1875, 133), who tested barley against hay (the nutritive ratio being 1 : 8·4). In the case of rice meal, the authors have less confidence in their own results, inasmuch as the high percentage of fat in Period 5 may have been prejudicial to the relatively young animals.

Tables showing the amounts of water consumed during the experiments, and the amounts of urine produced, are given in the original paper.

The gain in the weight of the two sheep during the 84 days the experiments lasted was 0·20 and 1·45 kilo. The results show that a sheep of the South Hanover district, weighing about 31·5 kilos. requires, at a temperature of 10·1°, the following amounts of food-constituents to retain its original condition:—Proteïn 74·1, fat 8·8, crude fibre 70·5, non-nitrogenous extract 301·4 grams.

With regard to the value of cellulose, the results of the experiments do not indicate any difference between it and the readily soluble carbohydrates as regards the saving of proteïds. N. H. J. M.

Chemical Theory of the Coagulation of the Blood. By M. ARTHUS and C. PAGÈS (*Compt. rend.*, **112**, 241—244).—If the soluble calcium compounds in blood are precipitated by adding an alkaline oxalate, the coagulation of the blood is prevented, but can take place if a soluble calcium salt is added. The action of the oxalates is quite different from that of such salts as sodium sulphate, magnesium sulphate, &c. The fibrinogen of the blood is not precipitated, and undergoes no change. From these facts and the results obtained by previous observers, the authors conclude that under the influence of the fibrin ferment, and *in presence of calcium salts*, the fibrinogen of the blood plasma is decomposed into two substances, namely, an insoluble, calciferous compound, fibrin, and a soluble compound, globulin, which coagulates at 64°. C. H. B.

Destruction of Sugar in Blood. By R. LÉPINE and BARRAL (*Compt. rend.*, **112**, 146—148; compare Abstr., 1890, 1172).—The activity of the glycolytic ferment in the blood of the dog increases as the temperature rises from 15° to 54°, but at the latter point it suddenly stops, although the physical condition of the blood does not differ appreciably from that at 52°, a temperature at which the ferment is very active.

At 39°, the defibrinated blood of a dog loses more sugar in winter than in summer, and it follows that the ferment is either more active or is present in greater quantity.

At 39°, the blood from the portal vein loses much more sugar than the blood from the splenic vein and from the arteries under identical conditions, the difference being at least 20 per cent. It follows that the ferment is excreted from the pancreas, not only by the lymphatics of the pancreas, but also in considerable quantity by the venous rootlets.

Even in a dog deprived of its pancreas, the destruction of the sugar did not cease, although reduced to about one-sixth of its normal amount. It would seem, therefore, that the ferment is derived from other organs as well as from the pancreas. C. H. B.

Muscular Work and Proteïd Metabolism. By D. N. PATON (*Lab. Reports, College of Physicians, Edin.*, **3**, 241—249).—The question of the influence of muscular work on proteïd metabolism has been recently reopened by Argutinsky (this vol., p. 350) and Krummacher (*ibid.*, p. 479). They found an increase in proteïd metabolism sufficient to account for no less than 75 to 100 per cent. of the amount of energy required to raise the weight of the body to the height ascended. These experiments were, however, unsatisfactory, as the work of forward progression, the movement of the arms, and the increased respiratory efforts are all left out of account. Both men, moreover, were on insufficient diet, and in bad condition, losing weight throughout the experiments. Munk also concludes from similar considerations that their results are of no value (*Centr. Med. Wiss.*, 1890, 738). Hirschfeld (*Virchow's Archiv*, **121**, 501) has recently published three similar experiments; his diet was sufficient, and no increase of the excretion of nitrogen followed muscular work.

In the present experiment, the diet was simple and carefully analysed, the work done consisted in raising a weight, and to this must be added a certain amount of walking exercise which is allowed for on the data given by Marez and Demeny (*Compt. rend.*, **101**, 905). With a slight amount of work, no increase occurred in the excretion of nitrogen; but when the work done was increased, especially after periods of comparative rest, the output was certainly increased. Thus the excretion of nitrogen on the four days preceding the work amounted to 60·144 grams, on the four days following the exercise to 61·3678, showing an increased excretion of 1·223 grams, equivalent to 7·949 grams of albumin, which is equal to 32·55 calories, or 13833·75 kilog. metres, or 85 per cent. of the energy required for the muscular work of ascending the stairs and raising the weight. W. D. H.

Electrolysis of Animal Tissues. By G. N. STEWART (*Lancet*, **2**, 1890, 1264; and *Studies from Physiol. Lab.*, *Owens College*, **1**, 124—177).—It was found that practically the whole of the conduction in animal tissues is electrolytic, and the electrolytes are principally the mineral salts, changes in the proteïds being produced by secondary electrolytic actions. In simple proteïd solutions, conduction occurs with great difficulty if salts are absent or present in small proportions. The effects on the proteïds themselves in saline solutions vary somewhat with the current density. Alkali-albumin is formed at the cathode, and acid-albumin at the anode; whilst in solutions of coagulable proteïds there is also coagulation at the latter pole. With a strong current, the proportion of coagulated proteïd to acid albumin is greater than with a weak current.

It was found that in bile and urine the conduction there also was chiefly due to electrolysis in the mineral, and not the organic, substances in those secretions. In blood, changes in the proteïds occur similar to those just mentioned. There is also a formation of acid-hæmatin (mixed with or preceded by methæmoglobin with certain strengths of current) and of alkali-hæmatin at the anode and cathode respectively. There is no evidence that hæmoglobin or any of its derivatives can act as an ion.

In muscle, the nuclei become apparent, and the sarcous substance granular at the anode; this is the appearance always produced by a weak acid. At the cathode, the fibres become more homogeneous. The chief chemical changes in the proteïds are an increase in the neutralisation precipitate of the aqueous extract, and a corresponding decrease of the globulin. At the anode, the neutralisation precipitate is increased, but the amount of globulin is more than correspondingly diminished, because part of this proteïd is coagulated. The effects of electrolysis on the salts of the muscle were studied by estimating the ash. Striking changes were found to occur which, if produced within the living body, would profoundly modify nutrition.

The antiseptic action of the current was studied in the case of micro-organisms, and it was found to occur chiefly, if not entirely, around the anode. An attempt is made to connect this knowledge with the application of electrolysis in surgery, and a further communication on the physiological aspects of the question is promised.

W. D. H.

Human Bile. By D. N. Paton and J. M. Balfour (*Lab. Reports, College of Physicians, Edin.*, **3**, 191—240).—The bile was collected from a woman who had had the operation of cholecystotomy performed for impacted gall-stone. The bile had a brownish-orange colour when fresh: it turned green after standing. It had an alkaline reaction. The urine was also collected daily, and the total nitrogen determined; its colour was usually high, and due to normal urobilin. Indican was abundant on several occasions. The fæces varied in colour from clay-white to slate-grey; they were offensive, and contained no biliary constituents. The nitrogen and fat in them were occasionally estimated. The following is the average of six quantitative analyses of the bile:—

Ether extract (cholesterol, lecithin, fat)	0·075	per cent.
Alcohol extract (bile salts, soaps, and some pigment)	0·349	,,
Mucin, pigments, and other organic substances insoluble in ether or alcohol	0·461	,,
Inorganic salts, insoluble....	0·003	,,
,, soluble	0·638	,,

Estimations of certain individual constituents gave the following results:—

Cholesterol	0·053
Lecithin and fat	0·009
Glycocholic acid	0·356
Taurocholic acid....	0·049
Fatty acids (from soaps)....	0·015

The following are the general conclusions drawn from this case relating to the physiology of bile secretion:—

1. The amount secreted varies greatly under the influence of many factors.

2. The introduction of biliary constituents within the alimentary canal has not so great an effect in increasing the bile flow as experiments on dogs would indicate.

3. The quantity of bile and of its solid constituents has probably been over estimated by previous observers.

4. The taking of food has no immediate effect in accelerating the flow of bile.

5. The flow of bile varies much during the 24 hours, being highest about midday, and lowest in the early morning.

6. The greatest amount of solids is produced in the liver during the

night. This is chiefly due to the organic constituents, the inorganic salts remaining fairly constant.

7. The amount of bile varies with the amount of fluid ingested.

8. The activity of metabolism has a distinct effect on the amount of bile solids produced, but not on the flow of bile.

9. Fever produces a marked and immediate fall both in the amount of bile and of its essential constituents. The mucin and inorganic salts remain unaltered.

10. Of the drugs used, sodium salicylate and calomel were most active in increasing the biliary flow: ox bile less markedly so.

11. The bile plays some part in promoting absorption of fat, but not on that of proteïds and carbohydrates.

12. The pressure under which bile is secreted is higher than the blood pressure in the capillaries of the liver.

13. The bile is doubtless an excretion rather than a secretion, for its only digestive action (that on fats) is not very important, 70 per cent. of the fat ingested being absorbed when no bile enters the intestine. The constituents of the bile which are discharged *per rectum* come probably from the blood corpuscles; a correspondence between the amount of bile solids produced and the nitrogen excreted in the urine supports the view of their close connection.

W. D. H.

Oxyhæmoglobin in the Bile. By R. STERN (*Virchow's Archiv*, **123**, 33—43).—Wertheimer and Meyer (Abstr., 1889, 636) and Filehne (*Virchow's Archiv*, **117**, 415) have described certain poisons which cause the appearance of oxyhæmoglobin in the bile. In the present research, care was taken to avoid admixture of the bile with blood from operative procedures, and also by examining the bile either while the animal was alive or immediately after death, to avoid a source of error pointed out by Wertheimer and Meyer, which consists in the fact that some hours after death some blood pigment diffuses into the gall bladder. In the case of human beings, in which many observations were made, it was not so easy to avoid this latter source of error, though the post-mortem examinations were performed as soon as possible after death.

The previous observers named found that the hæmoglobinocholia which they were able to produce by aromatic drugs in rabbits was not found to occur under the same conditions in dogs. It is here suggested that this may be due to a difference in the readiness with which hæmoglobin is decomposed in different species of animals (compare Krüger, Abstr., 1888, 510).

The chief experiments in the present research consisted in injecting small quantities of oxyhæmoglobin into the circulation of rabbits, and observing when it was discharged into the bile and into the urine. The following table gives the mean results :—

Quantity of hæmoglobin injected per kilo. of body weight.	Hæmoglobin in Bile.	Hæmoglobin in Urine.
0·468 gram.	Present.	Present.
0·073 „	Present.	Traces present.
0·061 „	Present.	Absent.
0·059 „	Present.	Absent.
0·025 „	Traces present.	Absent.
0·019 „	None present.	Absent.

In other words, small quantities of hæmoglobin appear in neither secretion as such, being changed into bile pigment; larger quantities readily pass into the bile, usually some hours after the injection, and still larger doses are necessary to produce hæmoglobinuria. Subcutaneous injections of hæmoglobin solutions produce the same change, but larger doses are necessary than when it is administered intravenously.

The application of this knowledge to pathology depends on the fact that certain micro-organisms, like the *Bacillus anthracis* and the bacillus of diphtheria, have the power of liberating hæmoglobin in the circulation, and in rabbits oxyhæmoglobin was found in the bile though not in the urine after infection with these pathogenic microbes.

The bile of a large number of corpses was then examined, and in cases of diphtheria, typhoid, and empyema the blood pigment was constantly found in the bile. In other pathological conditions, tuberculosis, scarlet fever, apoplexy, &c., oxyhæmoglobin was sometimes found; but in all cases the source of error previously alluded to could not be excluded. W. D. H.

Increased Output of Nitrogen in Cerebral Hyperthermia. Fever, and Artificial Overheating. By P. RICHTER (*Virchow's Archiv*, **123**, 158—165).—A careful comparison of three conditions was made in connection with the question of nitrogenous excreta and its relation to increased body temperature. The three conditions were: (1) the febrile state, associated with nervous injuries in which presumably the mechanism that normally regulates the body temperature is deranged; (2) continued fever; and (3) artificial heating of the body so that the body temperature is raised. In all three cases there was an increased output of nitrogen in the excreta as well as increased gaseous exchanges (intake of oxygen and output of carbonic anhydride) in the lungs. The general, far sweeping conclusion drawn is that, as in artificial overheating, so also in nervous hyperthermia, and, to a certain extent, in all fevers, and especially in some forms of fever, the increased production of heat (due to an increase of metabolic changes) is the result and not the cause of the elevated body temperature. W. D. H.

Excretion of Balsams in the Urine. By R. STOCKMAN (*Lab. Reports, College of Physicians, Edinburgh*, **3**, 65—69).—The research carried out on human beings and rabbits with the four balsams of the

British Pharmacopœia (balsam of Peru, balsam of Tolu, prepared storax, and benzoïn) is of interest, as use is made of these drugs in the treatment of tubercular disease, and nephritis is said to have been set up in certain cases as a result. It was found that balsam of Peru caused no disturbance of the kidneys, but the urine (if the dose given is large) gives a precipitate with nitric acid, as if albumin was present. The precipitate is, however, soluble in alcohol and in excess of acid, and no doubt it consists of the resin of the balsam, probably in combination with glycuronic acid. Prepared storax, which is used in the treatment of scabies as an ointment, causes a similar condition, which was mistaken by Unna (*Virchow's Archiv*, **74**, 424) for albuminuria. Treatment with benzoïn gave no positive results as, owing to the difficulty of dissolving it in suitable menstrua, it was impossible to give large doses. The same may be said for balsam of Tolu. In all cases, the urine contained a large excess of hippuric acid. W. D. H.

Hæmatoporphyrin in Urine. By E. SALKOWSKI (*Centr. med. Wiss.*, 1891, 129—130).—Three cases are briefly described of women patients who passed a dark pigment in their urine. The pigment was found to be hæmatoporphyrin, which was separated as a calcium compound; MacMunn (*Proc. Physiol. Soc.*, 1890, 13) and Ranking and Pardington (*Lancet*, ii, 1890, 607) have recorded similar cases. In the present instances, the phenomenon is attributed to the fact that sulphonal was being taken as a drug at the time. W. D. H.

Unusual Pigment in Urine. By V. HARLEY and S. TORUP (*Brit. Med. J.*, ii, 1890, 1169—1170).—Two cases are recorded of women who suffered from grave nervous symptoms (insomnia, coma, &c.), ending in death. They were treated with sulphonal and chloral, and passed urine of a port wine colour. The urine contained no albumin, sugar, bile, or blood. The abnormal urinary pigment is believed to be a precursory state of the normal urinary pigment, in fact, merely a less highly oxidised stage of it. W. D. H.

Note by Abstractor.—From the spectroscopic appearances described, and the general characters of the urine, there can be but little doubt that these were cases of hæmatoporphyrinuria (see preceding abstract).

Physiological Action of Saline Solutions and Various Drugs. By R. HEINZ (*Virchow's Archiv*, **122**, 100—124).—In the investigation of the physiological action of drugs, it is often necessary to dissolve these in saline solutions before introducing them subcutaneously or intravenously into the body of an animal. The strength of the saline solution used is by no means unimportant. It is especially unadvisable to use concentrated saline solutions, as it is found that strong solutions of sodium chloride, the salt chiefly used, produce changes in the blood, especially in its coloured corpuscles, and changes of the nature of inflammation, infarction, and hæmorrhage in the alimentary canal and elsewhere. For subcutaneous injection, more than a 5 per cent. solution of sodium chloride should be avoided, and for intravenous injection, "isotonic" solutions, or solutions but slightly hyperisotonic, should be employed.

Figures are given of the effect of a number of organic substances, chiefly derivatives and compounds of phenylhydrazine, on the red corpuscles of cold- and warm-blooded animals. The phenylhydrazine derivatives make the blood a brownish-green colour; spectroscopically, the bands of methæmoglobin are seen, the red corpuscles are shrunken; in the nucleated corpuscles of cold-blooded animals, the nucleus becomes oval, and the pigment collects around it in the same manner as when the corpuscles are treated with boric acid. In the non-nucleated red corpuscles of mammals, a brightly refracting globule is exuded, which adheres to the shrunken corpuscle, and is stainable a deep violet by methyl-violet.

With another category of organic substances (ammonia, diamines, hydroxylamine, amines, and amidines of the fatty and aromatic groups of compounds), the changes are somewhat different. The most characteristic change in nucleated red corpuscles is the appearance within them of numerous clear granules looking like vacuoles; these can be squeezed out of the corpuscles, and are found to be stainable by Bismarck-brown, and soluble in dilute hydrochloric acid, but not in dilute acetic acid, or in alcohol. In the non-nucleated discs of mammals, these little bodies are not formed, but the discs become mis-shapen and lose the greater part of their pigment in time.

The physiological action of pyridine is similar to that of piperidine, except that it acts more energetically. They both produce paralysis of the motor nerves, by their effect on the motor centres; there are also destructive changes in the blood corpuscles, and paralysis of the heart, especially in pyridine poisoning.

Quinoline and decahydroquinoline have analogous actions; they lead to a paralysis of central origin, a loss of excitability in the motor nerves, leaving the sensory nerve-endings and muscular substance almost intact; and, moreover, as with pyridine and piperidine, the non-hydrogenated substance quinoline is more powerful than the hydrogenated substance decahydroquinoline. W. D. H.

Physiological Action of Antipyretics. By P. Richter (*Virchow's Archiv*, **123**, 118—138).—The antipyretic action of kairine on animals with normal and febrile temperatures was investigated by calorimetric methods. The main result of the experiments is that the drug acts on the regulating mechanism which under normal circumstances keeps the body temperature at a fixed level. This is affected in the same manner, but with different degrees of intensity in normal and in febrile animals. The increase in the amount of heat lost is secondary, that is to say, it is dependent on the adjustment of the regulating apparatus; it is a means which assists the lowering of the body temperature, but is not the only cause of the antipyretic action of the drug. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Souring of Cream. By V. Storch (*Bied. Centr.*, **20**, 48—59; from *Tidskr. f. Landök.*, 1890, 352—416).—In order to ascertain the causes of certain defects in butter, especially "oily" butter, several samples were submitted to bacteriological analysis. The attempts to isolate an organism which produced the "oily" taste in butter were unsuccessful, but numerous fungi were found in butters with this defect, which were not found in others, and it is probable that these fungi are injurious. With regard to "tallowy" butter, a definite organism was found; it coagulates milk much as the usual souring-bacterium, which it also resembles in size and form. The turnip taste which butter sometimes has, although made from the milk of cows which receive no turnips in their food, is also probably due to a special micro-organism.

Tables are given showing the percentage numbers of defective butters under the headings "oily," "bitter," and butters with a "burnt taste," produced under a different systems of dairying.

In order to sterilise milk, heating at 107° for 5—10 minutes is not sufficient. Even a temperature of 120° for 10 minutes was in one case found not to have sterilised the milk; a pure cultivation of a small bacillus was obtained, whose thick, egg-shaped spores had resisted the high temperature.

Milk heated at 70° acquires a strong odour and taste. By discontinuous heating at this temperature, sterilisation may be effected.

Attempts were made to isolate a souring bacterium which produces the pure aromatic odour which well soured cream has. Bacteria were isolated from soured butter milk, and from two samples of butter, but the bacteria produced either only a slightly aromatic taste or none at all, although they all produced the right consistence and a pure acid taste.

Cream and butter from a farm distinguished for very aromatic butter were next tried, and the souring bacteria isolated. Of these, two (both from cream) were found always to produce the distinct aromatic taste. The one (No. 18) which also produced an especially agreeable, mild and pure acid taste was further examined, and is no doubt one source of butter aroma. On gelatin plates it forms small, pure white colonies which show a somewhat oval form. The temperature most favourable to it, is somewhat higher than that usually employed in dairies for souring. In shape, size, and mode of growth, the bacterium is in many respects similar to Pasteur's "ferment lactique"; but the power of motion, which the author's bacterium possesses, shows that it is not identical with Pasteur's ferment. The virulence of most of the souring bacteria is much weakened when they are kept in the same milk, but at once returns when the pure cultures are repeatedly inoculated in fresh milk. Souring bacteria which lose their virulence in one or two months when kept in the usual way may be kept more than a year when finely powdered calcium carbonate is added to the nutritive solution.

The amount of acid produced in milk by various souring bacteria was determined, and the results are given in tables. The difference in the acidity produced by the different bacteria was only slight; but the bacterium which also gives rise to the aromatic taste, &c., gave the least amount of acid. The greater part of the acid was formed in the first 24 hours, and the production ceased after six days. It was found that a loss of 0·656 per cent. of milk-sugar corresponds with a production of 0·635 per cent. of lactic acid. No evolution of gas ever took place.

The souring bacterium (No. 18) is capable of producing in milk-sugar solutions, free from fat and proteïds, and containing only a little peptone, the same aromatic taste which it gives rise to in milk or cream, so that the opinion, sometimes expressed, that this taste is due to volatile acids formed from butter fat, is erroneous.

The author proposes that in practice, fresh souring material should be prepared daily by means of pure cultivations. The danger of the contamination of butter with pathogenic bacteria would thus be much lessened. N. H. J. M.

Assimilation of Mineral Salts by Green Plants. By A. F. W. SCHÖMPER (? A. F. W. SCHIMPER) (*Bied. Centr.*, **20**, 69—70; from *Flora*, **73**, 207).—The nutritive salts of the soil do not at once reach the parts of the plants where they are wanted, but are generally stored up in the root stems and in the woody parts of the above-ground stems. The seeds contain the salts, especially phosphates, as organic compounds, which are, however, during germination, again split up. The power of plants of storing mineral substances differs much qualitatively as well as quantitatively. The object of lime is to convert the poisonous potassium oxalate, which is found in considerable amount, into calcium oxalate. The assimilation of nitric acid takes place in the green cells. Nitrogen migrates chiefly in the form of amides and amido-acids, which can be detected in the leaf parenchyma. N. H. J. M.

Influence of Internal Causes on the Presence of Starch in Leaves. By E. MER (*Compt. rend.*, **112**, 248—251).—The accumulation of starch in leaves of the Coniferæ is not dependent on the intensity of the illumination that particular leaves have received. In the case of the pines, firs, and Epiceæ, it is greatest in April and May; from June to mid-August the quantity is greatest in the young leaves, and is almost entirely localised in that face of the leaf which is in shadow. Sometimes the leaves in the shade contain more starch than those which are most exposed to sunlight. From the middle of August to the end of September, the quantity of starch in the leaves varies greatly with the species, but is always very low. In October the quantity is still low, but under favourable conditions of light increases somewhat, its distribution being very irregular. The quantity of starch that can accumulate in the leaves is determined by the ratio of the rate at which it is formed to the rate at which it is used up by the plant, also by the ease with which it can migrate into other parts of the plant, and by other causes at present not clearly made out.

C. H. B.

Action of the Diastase Ferment on Starch Grains within the Plant. By G. KRABBE (*Bied. Centr.*, **20**, 61—63; from *Jahrb. wiss. Bot.*, **21**, 520).—As opposed to the view that the diastase ferment penetrates into the substance of the starch grain, and extracts it like an acid, the author considers that even in the cases where channels are found in the grains, the starch remains unchanged outside the hollows which are formed. The particles of ferment consist, not of molecules but of groups of molecules, much too large to penetrate between the starch mycellæ. Diffusion and other experiments indicate that diastase has not the power of migrating from cell to cell, but it must always first be formed at its place of action. Attention is drawn to the sweetening of potatoes, which is caused by the activity of the protoplasm, and the using up of the sugar being only very slight at 0° to 6°, whilst the action of the diastase in converting starch into sugar continues, and causes an accumulation of sugar.

It is concluded that the action of diastase is a chemical and physical one, comparable with the action of solvents on crystals.

N. H. J. M.

Formation of Phloroglucinol in Plants. By T. WAAGE (*Chem. Centr.*, 1890, ii, 1017—1018; from *Pharm. Zeit.*, **35**, 694).—The author considers that the starch is converted in plant life into a monose, 1 mol. of water being absorbed. On the other hand, monose may lose 1 mol. of water forming starch, or 3 mols. of water forming a secondary, or pseudo-phloroglucinol, which forms a *trioxime*, $C_6H_6(NOH)_3$. The author has experimentally proved that dextrose is converted in the leaf into normal phloroglucinol, by placing one end of a leaf strip (cut through so that the liquid can enter the veins) in water, and the other in a solution of grape sugar. It was kept in the dark for six days, after which period ploroglucinol was found in the water. Moreover, phloroglucinol was not found in the chlorophyll, but only the cell-sap, and principally at those parts where the life-process was most energetic. The author considers that phloroglucinol combines with 1 mol. of carbonic anhydride, forming phloroglucinolcarboxylic acid,

$$C_6H_2(OH)_3{\cdot}COOH,$$

and that 2 mols. of this part with 1 mol. of water, forming diphloroglucinoldicarboxylic acid.

The author does not consider that phloroglucinol is a food to the plant, since, in autumn, when the leaves fall, it remains in them, and does not recede with the nitrogenous substance and the starch into the stem; on the other hand, he does not consider it a true excretory substance, since from it several substances, such as ethereal oils and sugary juices, are formed. From phloridzin, by the action, first of acid, and then of alkali, the author obtained glucose and phloretin, and from the latter, phloroglucinol and phloretic acid; and by similar means he obtained from quercitrin, isodulcitol and quercetin; and from the latter, phloroglucinol and quercetic acid. J. W. L.

Presence and Function of Sulphur in Plants. By Berthelot and G. André (*Compt. rend.*, **112**, 122—125).—The plants investigated were *Sinapis alba*, *Camelina sativa*, *Allium cepa*, *Lupinus alba*, *Urtica dioica*, *Tropæolum majus*, *Avena sativa*, the total sulphur, sulphates, organic sulphur, and volatile sulphur being determined in the seed, and in the plant during germination, flowering, and fructification. In the case of *Sinapis alba*, these determinations were made separately in the stalks, leaves, and other parts of the plant.

The total quantity of sulphur increases continually from germination to inflorescence, but the relative quantity is about one-third higher in the earlier stages of growth. The organic sulphur reaches a maximum when the plant is in flower, and afterwards decreases. Since organic sulphur is found in the roots, especially during the time of flowering, it is probable that the sulphur is not absorbed from the soil entirely in the form of sulphates. The proportion of the two forms of sulphur in the seeds varies considerably in different species. The final reduction of the proportion of organic sulphur is due partly to elimination in the form of volatile compounds, and partly to reoxidation during fructification. C. H. B.

Fats obtained from the Fungi Lactarius vellereus and L. piperatus. By Gérard (*J. Pharm.* [5], **23**, 7—12).—The fats yielded by these plants are chemically identical. They were found to contain oleïc and stearic acids, both in the free state and combined as glycerides; the volatile acids, formic, acetic, and butyric; some, cholesterol and lecithin. The cholesterol does not differ from animal cholesterol, and appears to be identical with *ergosterin* obtained by Tanret from ergot of rye. J. T.

Constituents of the Seed Pods of Pisum sativum and Phaseolus vulgaris. By A. Likiernik (*Ber.*, **24**, 187—188).—A compound has been isolated from the seed pods of *Pisum sativum* which agrees in properties with phytosterol.

From the seed pods of *Phaseolus vulgaris*, a mixture of two substances is obtained, which may be separated by fractional crystallisation from dilute alcohol; the more insoluble is termed *paraphytosterol*, the other *phasol*.

Paraphytosterol belongs to the cholesterol group, and crystallises with 1 mol. H_2O in broad, lustrous plates melting at 149—150°. In chloroform solution, the rotatory power is $[\alpha]_D = -44·1°$; the formula appears to be $C_{24}H_{40}O$, or $C_{26}H_{44}O$.

The *benzoate* crystallises from ether in dull, thin prisms.

Phasol, $C_{15}H_{24}O$, crystallises in small, lustrous, anhydrous plates, melts at 189—190°, and has a rotatory power $[\alpha]_D = +30·6°$; on treatment of a chloroform solution with sulphuric acid, a purple-red coloration is produced. Phasol appears to belong to the same homologous series as cupreol and quebrachol. J. B. T.

Root Nodules of the Pea. By A. Prazmowski (*Landw. Versuchs-Stat.*, **37**, 161—238, and **38**, 5—62).—The first paper commences with a review of the results of other investigators, and of the views held by them regarding root nodules. Schindler (*Bot. Centr.*, **18**, 84) was the first to suggest that the nodules might be symbiotic formations between the leguminous plant and soil organisms. Brunchorst (*Ber. bot. Ges.*, **3**) considers the nodules to be normal formations, in which albuminous substances in the form of bacteroïds are accumulated; that the bacteroïds serve the plant in some way, and that when they have performed their service they are resorbed by the plant. These views, which are generally accepted, are founded on microscopical observations only. Beyerinck (*Bot. Zeit.*, **46**) succeeded in cultivating in artificial media, bacteria obtained from the nodules of several *Leguminosæ*, and concluded that these bacteria give rise to the production of nodules; and further, that the bacteria within the nodules, after increasing in numbers, become converted under the influence of the cell plasma into bacteroïds (that is, metamorphic bacteria), which have lost the power of propagation, and which are finally resorbed by the plant.

In the author's first experiments (1885), peas and beans were grown in rich garden soil, in the same soil sterilised, and in the sterilised soil with the addition of garden soil extract. Nodules appeared in the roots of all the plants except those of the sterilised and non-infected soil. Other experiments, in which the same plants were grown in washed sand, under different conditions as regards sterilising, &c., gave similar results. Pure cultivations of the nodule organisms were then made, and peas grown in sterilised sand infected with them; in every case numerous nodules were produced. The bacteria, when in contact with the cell plasm of the roots, undergo successive changes; first, they assume the forked shape of the bacteroïds; at a later period the substance of the bacteroïds is found to contain strongly refractive grains (Lundstroem, *Bot. Centr.*, **33**, and Beyerinck, *Bot. Zeit.*, 1888, 735), which are shown by their behaviour towards reagents to have the properties of proteïds. This albuminous substance is subsequently resorbed by the plant. But only a portion of the bacteria undergo these changes; others multiply, and on the death of the plant, or when the nodule is injured by insects, &c., return in increased numbers to the soil. The production of the proteïds and their resorption by the plant indicate that the bacteria are of use to the plant in supplying certain necessary food-constituents. It was observed that the nodules of plants growing in rich soil retain their freshness and red colour to a much later period than those of plants growing in sand.

The second paper commences with an account of the different ideas held regarding the biological meaning of the root nodules. Whilst Woronin, Ericksson, Kny, Frank (1879), and Prillieux held them to be a kind of disease, all other investigators associated the existence of the nodules with the fact that leguminous plants have the power of acquiring nitrogen from sources which are not available to other plants. De Vries, on the strength of microscopical observations, assumed them to be organs in which nitrogenous compounds taken up by the leaves and roots are converted into proteïds, a view also held by Schindler (*J. Landw.*, **33**). According to Brunchorst (*loc. cit.*), the nodules convert the organic matter of the soil into proteïds; inorganic nitrogen compounds are assimilated by the plant without their intervention. Tschirch (*deut. landw. Presse.*, 1886) thinks the nodules store up albumin which is afterwards required by the plant when ripening. He attributes the enriching of surface soil in nitrogen by the growth of leguminous plants to the bringing up of subsoil nitrogen collected in the root-nodules. The author next discusses Hellriegel's results, which he accepts, as far as they go, whilst maintaining that some of his conclusions, which may be correct, cannot be considered as final without further evidence. In the author's experiments, sterilised sand was used, and great care was taken to maintain the state of sterilisation throughout the experiment. The plants were infected with pure cultivation of nodule-bacteria, grown in non-nitrogenous nutritive solutions. The pots had well-fitting covers, with four holes: a centre hole for the plant, and three others, into which glass tubes were cemented for supplying nutritive solution and sterilised air. One of the chief points of interest during growth was the observation that about 2—3 weeks after sowing the infected plants became unhealthy-looking, as compared with the non-infected plants; but after the fifth week, the infected plants became the stronger, and from this time to the end of the experiment remained healthy. In the water-culture experiments described below, it was found that the unhealthy period in the growth of the infected plants was coincident with the first appearance of nodules, and that the period of renewed vigour was coincident with the first emptying of the nodules. Returning to the sand-culture experiments, nodules were found in the roots of all the infected plants, and *vice versâ*. The sand was examined at the end of the experiments, to ascertain whether other organisms than those added had got in. It was found that in the first series of experiments (pots 1 to 4 in table), owing to some defect, all the pots contained foreign organisms. In the second series (pots 5 to 9), the sand of pots 5, 6, and 8 remained free from foreign organisms, and that of 3 and 5 contained only a mould-fungus as impurity. There were fewer nodules where nitrate was applied than where not, but the nodules in the nitrate pots were better formed than the others.

The following table shows the amount of produce and the initial and final amounts of nitrogen in the sand culture experiments:—

	Dry produce (grams).	Length of stems (cm.).	Nitrogen.				
			Seeds sown.	Above ground growth.	Roots.	Whole plant.	Gain* or loss.
1. Not infected; nitrate......	4·6310	106·7	0·012	0·1263	0·0080	0·1343	?
2. Infected; nitrate.........	6·0486	112·0	0·012	0·1688	0·0162	0·1850	?
3. Not infected..	1·1660	97·7	0·012	0·0090	0·0042	0·0132	0·0012
4. Infected......	3·5445	109·3	0·012	0·0680	0·0146	0·0826	0·0706
5. Not infected; nitrate......	3·5492	103·2	0·009	0·0827	0·0065	0·0892	?
6. Infected; nitrate.........	5·2380	108·6	0·009	0·1445	0·0134	0·1579	?
7. Not infected..	0·4124	36·4	0·009	0·0051	0·0021	0·0072	−0·0018
8. Infected......	2·4755	92·0	0·009	0·0485	0·0098	0·0583	0·0493
9. ,, ...	1·6324	69·8	0·009	0·0319	0·0078	0·0397	0·0277

The water-culture experiments were made especially to test the accuracy of Brunchorst's view, that in water-culture the nodules have no function, an opinion which Hellriegel was also inclined to adopt (*Zeits. Ver. Rübenzuck.-Ind.*, 1888, 172). The results (water-culture) of the experiments do not support this view, being similar to those of the sand-culture experiments, although the assimilation of nitrogen was less than in sand. The numerical results are as follows:—

	Dry produce (grams).	Length of stem (cm.).	Nitrogen (grams).		
			Seeds sown.	Total produce.	Gain or loss.
1. Infected; nitrate...	4·9383	112·6	0·0090	0·1437	?
2. Not infected; nitrate	6·1436	132·8	0·0090	0·1746	?
3. Infected; nitrate...	4·5444	116·0	0·0090	0·1436	?
4. Not infected; nitrate	6·0133	132·8	0·0090	0·1914	?
5. ,, no nitrate.............	0·4162	36·6	0·0090	0·0090	0·0000
6. Not infected; no nitrate.............	0·4721	45·0	0·0090	0·0085	−0·0005
8. Infected; no nitrate	1·0742	93·0	0·0090	0·0264	0·0174
9. ,, ,,	2·2739	103·9	0·0090	0·0825	0·0735
10. ,, ,,	1·0826	88·4	0·0090	0·0321	0·0231
11. ,, ,,	1·1832	102·8	0·0090	0·0275	0·0185

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* With regard to the pots which had nitrate, although the amount of nitrate in the nutritive solution is given, the exact amount of solution actually used is not. Moreover, the amount of nitrogen in the sand at the end of the experiment was not determined, so that the gain of nitrogen or loss (if any) cannot be ascertained.—N. H. J. M.

The most important conclusions are the following:—

1. The root nodules are symbiotic formations, which derive benefit from the plants by obtaining nourishment from them, and are thus enabled to propagate themselves, and on the death of the plant to return in greatly increased numbers to the soil.

2. The symbiosis is of use to the plant by enabling it, under the influence of the bacteria, to feed on atmospheric elementary nitrogen.

3. Inasmuch as only plants provided with nodules can acquire nitrogen from the free nitrogen in the air, it follows that the assimilation takes place with the intervention of the nodule bacteria.

4. The coincidence of the recovery of the infected plant from its state of weakness with the emptying of the oldest nodules, taken together with the changes which the bacteria were found to undergo within the nodules, indicate that the plant only derives benefit from the symbiosis when it has overpowered the bacteria, and that the resorption of the products of the bacteria is the main cause of the increased production of the plants.

5. The resorption of the bacteroïds is the means by which the plant obtains atmospheric nitrogen.

6. Starch is present in the nodules in considerable quantity, as long as they possess vitality, and is directly taken up by the bacteria; it is probable that the bacteria are built up from this starch and elementary nitrogen.

7. In the absence of other sources, the nodule-bacteria (in pure cultivations) are able to assimilate free nitrogen, although to a much less extent than when in symbiosis with the plant (compare this vol., p. 353).

In a postscript the author criticises Frank's paper "On the Fungus-symbiosis of the Leguminosæ" (*Ber. deut. bot. Ges.*, **7**).

N. H. J. M.

Nitrogen Compounds in Vegetable Soils. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **112**, 189—195).—The authors have subjected vegetable soil to the action of acids and alkalis of various degrees of concentration for various periods of time. The soil used contained 19·10 grams of organic carbon and 1·669 grams of nitrogen per kilo., and if the nitrogen is regarded as existing in the soil in the form of proteïd compounds, the particular soil contained approximately 1 part of proteïds to 3 parts of humous compounds.

The action of cold concentrated aqueous potash indicated the existence of two groups of nitrogen compounds, one being much more easily decomposed than the other. The action of warm, dilute, aqueous potash results in a continual evolution of ammonia. In 26 hours at 100°, the alkali made 93·6 per cent. of the nitrogen soluble. Practically the same result was obtained by first treating with alkali, and afterwards with acid, and a slightly lower result by the action of acid followed by alkali. It would seem that several reactions take place simultaneously under the influence of the alkali. The nitrogen compounds at first split up and become soluble, but when the action is prolonged, the soluble products gradually lose nitrogen in the form of ammonia or soluble amides, and again form insoluble nitrogen compounds. The latter are not stable, but gradually decompose and again become soluble. C. H. B.

Volatile Nitrogen Compounds evolved from Vegetable Soils. By BERTHELOT (*Compt. rend.*, **112**, 195—197).—Clay soils kept moistened gradually lose nitrogen in the form of volatile products, but if the same soil is kept dry, the loss, although recognisable, is very much smaller. The nitrogen evolved in the form of volatile nitrogen compounds is greater than that evolved at the same time in the form of ammonia, a result contrary to that obtained with vegetable soils. It is probable that the evolution of volatile nitrogen compounds is intimately connected with the life of microbes or low vegetable organisms. C. H. B.

Formation and Properties of Humus. By P. A. KOSTYTCHEFF (*Ann. Agronom.*, **17**, 17—38; from *Trav. Soc. Naturalistes St. Petersburg*, **20**, 1889).—The chief results of the author's study of the black soils of Russia are discussed in this paper. The decay of vegetable matter is brought about by attacks of moulds and bacteria, the former alone causing the production of dark-coloured matters. A characteristic of humus is its richness in nitrogen, the humus of the black Russian soils containing from 4·00 to 6·65 per cent. of that element, whereas meadow hay contains only 1·62 per cent., and clover in flower 2·00. When some hay from this land (composed of *Festuca ovina* and *Koeleria cristata*), containing 100 parts dry matter, was moistened with 75 parts of water and allowed to decay under a bell-glass, air being injected every day, it was found that in six months the dry residual matter weighed only 62·25 parts. There was no loss of nitrogen, 1·2711 parts being found as against 1·2700 at the commencement, but the percentage of nitrogen had risen from 1·27 to 2·04. Similar experiments made with oak, elm, and other leaves gave analogous results; little or no ammonia is formed, and no nitric acid, and the loss of nitrogen is in general *nil*. As hay and leaves contain proteïds, and these quickly decompose with production of ammonia, it follows that this ammonia must be reconverted into other forms, and this is done by the agency of the living organisms, which find their nourishment in the decaying matter. The nitrogen is in fact reconverted into proteïd compounds, and not into simpler combinations; thus, of the 2·04 per cent. of total nitrogen found in the decomposed hay, 1·893 was present as proteïd, and only 0·149 per cent. as amidated compounds. Ammonia and amides when formed serve as nutriment to moulds, in the protoplasm of which their nitrogen is stored up, and this, decomposing in its turn, serves as food to bacteria, which still retain the nitrogen in proteïd combinations. Sometimes, as in decaying oak leaves, the form of the leaf is preserved, but almost the whole structure is transformed into a mass of ramifying and interlacing mycelium. The soil, with its estimated 60 millions of organisms per gram, must contain much nitrogen in the proteïd form, and one set or other of organisms will predominate according to variation in the conditions; thus, if soil is moistened and kept under a bell-glass, masses of mould are quickly produced throughout. In general, the first development in decaying vegetable matter is that of bacteria, the reaction of the medium becoming acid; then follows the decay of these, the ammonia produced neutralising the acid, and moulds growing in the neutral medium; afterwards bacteria and moulds develope together. Thus humus always contains easily decomposable matter, and consequently the rate of decomposition observed at any period of the decay is nearly the same. Experiments on the rapidity of decomposition of humus from the black soils and humus from soils further north, made by moistening equal weights to an equal extent and measuring the carbonic anhydride produced *per diem*, show that the rate of decomposition is the same in each. In humus produced above the water level, all trace of vegetable structure is destroyed by the leaves being gnawed and passed through the bodies of earthworms, caterpillars, wireworms, &c.; under the water level, the vegetable structure is preserved, and peat results. Experiments with dead leaves pulverised by the action of these animals, in comparison with the same leaves not attacked by them, show that little or no influence on the rate of decay results from their action. After passing through their bodies, the organic matter is still fit to nourish moulds and bacteria, and when these have multiplied sufficiently to accumulate a fresh stock of protoplasm, earthworms, &c., attack it again, and so destroy all trace of structure. The soil of the black lands is permeable to a small depth only by water, and this circumstance retards decomposition and accounts for the accumulation of humus. The decay of humus is fastest in the best drained and most open soils; for this reason the presence of clay in a soil promotes accumulation of humus. Woods promote drainage by loosening the soil and abstracting water, and hence in plantations accumulation of humus is retarded, and the earth becomes lighter in colour. Inferior organisms are the means of diffusing organic matter throughout the soil; the mycelia of fungi, for instance, growing on a dead root, ramify laterally, and thus carry organic matter a little way outward; succeeding organisms extend this action, and the soil becomes darkened in proportion. The humic acid of the black earth is almost exclusively in combination with lime; this lime is, according to the author, carried to the insoluble humus as acid carbonate dissolved in water, and the acid carbonate is decomposed by contact with the moist humus. To the observation that vegetable matter is blackened under the attacks of moulds and not of bacteria, the author adds that some fungi have the power of blackening humus, but in other cases they simply change the reaction from acid to alkaline, when the blackening is produced by atmospheric oxidation, as in the similar case of pyrogallol.

J. M. H. M.

Economy of Phosphoric Acid in the Growth of Beetroot. By M. MAERCKER (*Bied. Centr.*, **20**, 4—11; from *Magd. Zeit.*, 1890). —The object of the paper is to show the fallacy of the view that in the growth of beetroot heavy manuring with phosphates is necessary in order to compensate for the amounts removed by the crop. In the first place, beetroot is a crop which does not require a great amount of phosphate; an average crop will withdraw from the soil 23·8 lbs. per acre; an average potato crop removes 28 lbs. per acre. Then, again, by far the greater part of the phosphate so taken up will be returned to the soil in the form of diffusion-residues, &c. As much as 91·1 per cent. may be returned. From examples given, it is shown that the average actual loss of phosphoric acid, that is, the amount removed by the crop minus that contained in the waste products which are returned from the sugar works, is about 10·6 to 12·3 lbs. per acre. This is very nearly compensated for by keeping cattle. One beast, consuming 5·5 lbs. of such food as oil cake and rice meal, &c., will yield 50 lbs. of phosphoric acid yearly. At the rate of one beast to five acres, this will correspond with 10 lbs. per acre. A further amount of phosphates will be derived from the hay consumed. It is thus seen that the large amounts of phosphates usually applied are unnecessary. There is no evidence to show that the excess of phosphoric acid has any effect on the quality of the roots.

The usual manuring with farmyard manure gives more phosphoric acid than the beetroot removes, and any further amount of phosphates added must be useless.

Extensive experiments are being made at the author's suggestion, and, until further evidence is obtained, he proposes that 17·6 lbs. of soluble phosphoric acid per acre should be given, except when the farmyard manure is preserved by phosphate gypsum.

With regard to the preservation of farmyard manure, phosphoric acid should be much more extensively employed. The loss of nitrogen from one head of cattle in a beetroot farm may be as much as corresponds with 2·70 cwt. of Chili saltpetre; 60·5 lbs. of phosphoric acid is sufficient to prevent this loss. With the average number of cattle (one to 5 acres), and the average loss of phosphoric acid (10·6—12·3 lbs. per acre), it happens that for the preservation of the farmyard manure exactly the same amount of phosphoric acid is required as is contained in the beetroot products which are sold.

N. H. J. M.

Analytical Chemistry.

Weighing Dried Filters. By F. Rüdorff (*Zeit. ang. Chem.*, 1890, 633).—The filters are dried in cylindrical vessels 75 mm. high and 34 mm. in diameter, with ground caps. After 30 minutes in the oven, the vessel is removed, capped, and allowed to cool without using a desiccator for exactly 30 minutes, the last 10 minutes being in the balance case. After collecting the precipitate, it is dried at 100° in the funnel, and then for 30 minutes in the same way as the empty filter. A constant weight is very soon obtained.

M. J. S.

A New Method of Estimating Uncombined Hydrochloric Acid in Gastric Juice. By A. Jolles (*Monatsh.*, **11**, 472—481).—

The fluorescence of a neutral solution of eosin is scarcely affected by the presence of considerable quantities of organic acids, whilst it is instantly removed by the addition of only a very minute quantity of hydrochloric acid. On spectroscopic examination, the neutral solution of eosin shows two black bands in the blue-green portion of the spectrum; these bands are greatly intensified in presence of alkalis, but if a few milligrams of hydrochloric acid is added to the solution they instantly disappear, whilst they are, however, unaffected by the addition of several grams of lactic, butyric, acetic, or formic acids.

The author makes use of the preceding facts in the following way:—1 c.c. of a solution of eosin (0·01 gram) in water (100 c.c.) is added to 100 c.c. of the solution under investigation, and the mixture titrated against aqueous alkali in a vessel with plain, parallel sides, so that the formation of the black bands may be spectroscopically determined. The quantity of hydrochloric acid, expressed in milligrams, contained in the solution which has been titrated is given by the equation $x = n . a + c$, where n is the number of c.c. of alkali added, a the hydrochloric acid in milligrams which neutralises 1 c.c. of the alkali solution, and c a constant, depending on the thickness of the layer of the fluid and the concentration of the eosin solution used. When the solution is 40 mm. in depth, and contains the above given quantity of eosin, the constant is 20; that is to say, the addition of 20 milligrams of hydrochloric acid is necessary in order to make the absorption-bands disappear in a solution containing one-tenth of a milligram of eosin in 100 c.c. of water. The delicacy of the method is not affected by the presence of chlorides or phosphates, albumin, peptones, pepsin, or by lactic, butyric, acetic, or formic acid. In presence of these substances, so small a quantity of hydrochloric acid as 10 milligrams (0·01 per cent.) can be estimated with precision. G. T. M.

Potassium Iodate as Original Standard for Iodometry, Acidimetry, and Alkalimetry. By M. Gröger (*Zeit. ang. Chem.*, 1890, 385—386, see this vol. p. 360).—The facility with which pure potassium iodate is prepared renders it an admirable basis for iodometric analysis. Sublimed iodine is dissolved in hot, pure, moderately strong potash as long as it does not colour the solution. The liquid is evaporated to dryness, and the residue exhausted with alcohol. The undissolved portion is repeatedly crystallised from hot water, until it no longer affects sensitive litmus paper, or gives a blue colour with sulphuric acid and starch. The alcoholic solution is used for the preparation of potassium iodide; for this purpose it is evaporated to dryness, the residue dissolved in water, and iodine added to strong yellow coloration; hydrogen sulphide is then passed through the liquid, the filtered solution evaporated, and the iodide crystallised until pure. A permanent iodine solution for standardising thiosulphate may be made by dissolving accurately weighed iodine in an excess of pure potash, and diluting to a known volume. The solution can be preserved unchanged, and the iodine liberated at any time by adding excess of acid. M. J. S.

Potassium Bromide as Indicator in Chlorimetry. By G. Denigès (*J. Pharm.* [5], **23**, 101—103).—To avoid the use of alkaline solutions of arsenious anhydride, which do not remain constant, the more permanent hydrochloric solution may be prepared thus:—To 4·44 grams of arsenious anhydride 10 c.c. of soap solution are added and 100 c.c. of water; after a few minutes contact and agitation, the solution is complete in the cold; 500 c.c. of water and 100 c.c. of hydrochloric acid are then added and the mixture shaken again; finally it is made up to 1 litre, and again shaken. To make an estimation, 10 c.c. of the standard solution is placed in a flask, some drops of a concentrated potassium bromide solution added, and then the chlorine solution until a slight yellow tint just persists. This is much more convenient than the addition of sulphate of indigo.

J. T.

Technical Valuation of Bleaching Powder. By L. Vanino (*Zeit. ang. Chem.*, 1890, 509—510).—A rapid and fairly accurate estimation of the value of bleaching powder can be obtained by treatment with hydrogen peroxide, causing the oxygen evolved to displace water from a receiver, and measuring the water expelled. The weighed substance (2 grams), finely ground with water, is placed in a small flask; the hydrogen peroxide in a stopcock bulb, of which both the upper and lower ends are connected with the flask, so that no alteration of volume occurs when the liquid is admitted to the flask. The gas-evolution tube is connected with one neck of a Woulff's bottle full of water. Through the second neck passes a thistle funnel reaching nearly to the bottom of the bottle. Through a tubulure near the bottom passes a tube which, being bent at right angles, can be depressed by rotation in the cork until water begins to escape. On mixing the hydrogen peroxide with the bleaching powder, a quantity of water flows out equal in volume to the oxygen liberated. The tables published by the author (this vol., p. 246) allow the percentage of oxygen or chlorine to be read off without calculation.

M. J. S.

Estimation of Fluorine. By H. Offermann (*Zeit. ang. Chem.*, 1890, 615—618).—The author gives a somewhat full recapitulation of the methods hitherto proposed, and then describes the following process, which, unlike some older ones, is equally serviceable when organic substances, carbonates, or chlorides are present. It is based on the expulsion of the fluorine as silicon fluoride, which, being then decomposed by water, yields hydrofluosilicic acid, which can be titrated with an alkali. The substance is mixed with 15 parts ignited quartz powder, and placed in a 200 c.c. flask furnished with tubes for the admission of air and escape of gas, and with a funnel tube for introducing sulphuric acid. Air, dried and freed from carbonic anhydride, is passed into the flask at the rate of about two bubbles per second. The escaping gases pass over sulphuric acid in a second similar flask, in which a thermometer is inserted. Both flasks stand on the same hot plate, and are heated to 150—160°. The gases next pass through an empty U-tube, then through one containing fused calcium chloride and pumice saturated with anhydrous copper sulphate, and thence through a tube reaching to the bottom of a beaker, containing enough mercury to form a lute, and about 150 c.c. of water. The tube is liable to get stopped up. When the decomposition is complete, cochineal tincture is added to the liquid in the beaker and then standard alkali to a distinct alkaline reaction. 1 c.c. of normal alkali equals 0·019 gram of fluorine. M. J. S.

Gasometric Absorption of Oxygen. By L. L. de Koninck (*Zeit. ang. Chem.*, 1890, 727—728).—A solution of ferrous tartrate in excess of alkali absorbs oxygen with great rapidity, and is free from the inconveniences of many of the reagents proposed for that purpose. Three solutions are made, containing: (A) 40 grams of crystallised ferrous sulphate; (B) 30 grams of sodium potassium tartrate; (C) 60 grams of potash, each made up to 100 c.c. with water. One volume of A is poured into five volumes of B, and then one volume of C is added. A clear solution is thus obtained, which, when used in a Hempel's gas burette, absorbed the oxygen from 50 c.c. of air completely in four minutes, and in four experiments gave results comprised between 20·8 and 21·2 volumes per cent. M. J. S.

Estimation of Oxygen Dissolved in Water. By G. Linossier (*J. Pharm.* [5], **23**, 103—106).—The oxygen is absorbed by ferrous tartrate in alkaline solution, phenosafranin being used as indicator. A 500 c.c. flask, provided with a glass tap at the bottom, is charged with about 400 c.c. of mercury, 20 c.c. of sodium hydroxide solution of 36° B, 20 c.c. of a 20 per cent. solution of potassium sodium tartrate, a drop or two of alcoholic solution of pure phenosafranin, and finally water, to completely fill it. A caoutchouc stopper with two holes is placed in the neck, care being taken to exclude all air bubbles, and in one of the holes is inserted the jet of a burette previously completely filled below the stop-cock with standardised ferrous sulphate, and the other hole receives the tube of a stoppered funnel, the tube of which has been primed with the water to be examined. The whole should be perfectly tight, so that on opening the lower stop-cock no mercury runs out. Ferrous solution is now added drop by drop, until the rose tint just disappears; then 50 c.c. of the sample is placed in the funnel and passed carefully into the flask, and ferrous solution is again added to the same point as before. After the apparatus is once prepared, several estimations can be successively made without renewing the solutions contained in the flask; a fresh portion of the sample is added and more ferrous sulphate until the mercury is run out. Three estimations of the same sample should be made and the last one taken. To standardise the ferrous solution, water which has been in prolonged contact with air should be employed; when its temperature and the height of the barometer are known, the amount of oxygen dissolved can be obtained from the known solubility of oxygen. A convenient solution contains 3 grams of ferrous sulphate and 10 c.c. of sulphuric acid per litre. Nitrates and nitrites do not affect the result. Substances like glucose which exert a strong reducing action in alkaline solution are the only obstacles; the results are not affected by the addition of urine, albumin, or infusion of vegetable earth. J. T.

Volumetric Estimation of Sulphur Dichloride. By G. A. Le Roy (*Chem. Centr.*, 1890, ii, 1027; from *Mon. Sci.* [4], **4**, 1115—1116).—The following method is recommended by the author:—A weighed or measured quantity of the sulphur dichloride of commerce is added to a measured volume of sodium hydroxide of known strength. The dichloride is decomposed into sodium sulphide, thiosulphate, sulphite, sulphate, and chloride, and free sulphur. The latter is readily dissolved by boiling the alkaline liquid. It is then cooled and hydrogen peroxide added, and the liquid gently warmed, whereby the sulphur and lower sulphur compounds of sodium are oxidised to sulphate. The excess of hydrogen dioxide is destroyed by boiling. The excess of alkali is now determined volumetrically, as also the chlorine, from which data the amount of sulphate corresponding with the sulphur in the sulphur dichloride is calculated.

J. W. L.

Purification of Sulphuric Acid for Kjeldahl's Process. By G. Lunge (*Zeit. ang. Chem.*, 1890, 447—448).—The success obtained by Meldola and Moritz in purifying sulphuric acid from ammonia by heating with potassium nitrite (Abstr., 1888, 628) was due to their using a quantity of nitrite almost exactly equivalent to the ammonia to be removed, so that no excess of nitrogen trioxide remained to be boiled out. The author shows by fresh experiments, as well as by reference to the known facts of sulphuric acid manufacture, that nitrogen trioxide cannot be boiled out from concentrated sulphuric acid, but, in consequence of the formation of the very stable nitrosyl sulphate, actually concentrates in the residue left after boiling down the strong acid. M. J. S.

Estimation of Nitric Nitrogen by Aluminium. By A. Stutzer (*Zeit. ang. Chem.*, 1890, 695).—The conversion of nitric acid into ammonia by the action of aluminium and an alkali is one of the most convenient modes of estimating it, but it fails altogether with certain specimens of aluminium, which, there is reason to believe, are not made by the use of sodium. It is suggested that there may be traces of sodium in the aluminium made by the older process, and that their presence may be a condition of its suitability. M. J. S.

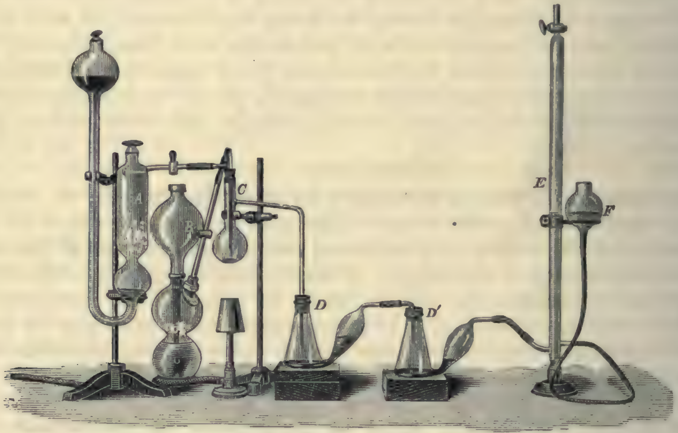
Estimation of Nitric Acid by Reduction to Ammonia. By K. Ulsch (*Chem. Centr.*, 1890, ii, 926—927).—The nitric acid is reduced by means of finely divided iron and dilute sulphuric acid. Not more than 0·5 gram of nitrate is introduced into a half-litre flask, dissolved in 25 c.c. of water and 10 c.c. of dilute (2 : 1) sulphuric acid and 5 grams of *ferrum hydrogenio reductum* added. The flask is then gently heated with a small flame, which, as the reaction moderates, is increased so that after about four minutes from the commencement the liquid is brought to boiling.

During the reaction, the neck of the flask is closed by a loose, hollow, pear-shaped glass stopper, containing about 25 c.c. of water, which acts as a condenser.

After the reduction, 50 c.c. of water and 20 c.c. of aqueous soda (sp. gr. 1·25) are added, and the ammonia distilled off. The whole process occupies from 15 to 20 minutes. The results are as follows: of six determinations of potassium nitrate, the highest was 13·89, the lowest 13·82 per cent. of nitrogen (theory = 13·86); of four determinations of sodium nitrate, the highest was 16·52, the lowest 16·43 per cent. of nitrogen (calculated 16·47); two determinations with barium nitrate gave 10·65 and 10·60 per cent. of nitrogen (calculated 10·73). Hydrochloric acid, as a substitute for sulphuric acid in the reduction process, does not give such accurate results, although the presence of chlorides does not seem to affect the accuracy at all.

J. W. L.

Iodometric Estimation of Nitrates and Chlorates. By L. L. De Koninck and A. Nihoul (*Zeit. ang. Chem.*, 1890, 477—481).—When a nitrate is distilled with a sufficient excess of hydrochloric acid of the highest concentration, the metal is wholly converted into chloride, all the nitrogen is given off as nitric oxide, and the remainder of the oxygen is represented by an equivalent quantity of chlorine, which can be estimated by absorption in potassium iodide and titration of the liberated iodine. The vessel A is for the generation of hydrogen chloride by the action of concentrated sulphuric acid on ammonium chloride (Abstr., 1881, 138). B is for generating carbonic anhydride, which must be perfectly free from air. The substance is placed in C with a sufficient, but not excessive, quantity of water (2—3 c.c. per decigram). Potassium iodide, of which too great an excess should not be used, is placed in the Volhardt absorbers D, D′, and the end tube is either connected with the Schiff's azotometer E, filled with strong potash, in which the nitric oxide may be measured as a control, or is dipped under mercury. The air is now completely expelled from the apparatus, and hydrogen chloride is then passed into C until the water is saturated. A slow stream of both gases is maintained, and the contents of C are boiled until the yellow colour of the nitrosyl and nitroxyl chlorides has disappeared.



The contents of C may even be distilled to dryness. The last traces of chlorine are then driven over by a more rapid current of gas, and the iodine in D and D′ is forthwith titrated by thiosulphate. Since differences corresponding with 0·1 c.c. of N/100 thiosulphate (equal to 0·02096 milligram of nitric acid) can be estimated, the process is applicable to very small as well as large quantities of nitrates. The presence of chlorides and bromides is not injurious. When iodides are present, the residue in C should be added to the solutions in D before titrating. Chlorates can be assayed by the same process.

M. J. S.

Estimation of Phosphoric Acid in Urine. By B. GUILLAUME-GENTIL (*Chem. Centr.*, 1890, ii, 893; from *Schweiz. Wochenschr. Pharm.*, **28**, 327—332).—The author recommends the estimation of the phosphoric acid in urine by precipitating it with magnesia mixture in a graduated tube; from the volume of the precipitate, the amount of the phosphoric acid is calculated. J. W. L.

Detection and Estimation of Boric Acid in Milk and Cream. By C. E. CASSAL (*Analyst*, **15**, 230—232).—The usual tests suffice for the detection of boric acid and borates in milk and cream, but for their estimation the milk or cream is rendered alkaline, evaporated and incinerated, and successive small quantities of methyl alcohol are distilled from the ash previously acidified with acetic acid. The distillate is collected on a known quantity of ignited lime, which is subsequently re-ignited and reweighed: the increase in weight is boric acid. D. A. L.

New Method for Decomposing Silicates. By P. JANNASCH (*Ber.*, **24**, 273—278).—In order to obviate the necessity of fusion with sodium carbonate, and, in estimating the alkalis, of solution with hydrofluoric acid and sulphuric acid, in the case of those silicates which are incompletely decomposed by hydrochloric acid under ordinary conditions, the author recommends that the finely-divided silicate should be heated at 190—200° with hydrochloric acid (4 : 1) for 10 to 12 hours. The substance and the acid are placed in a platinum tube (a diagram of which is given), closed with a platinum capsule, and enclosed in a sealed glass tube also containing hydrochloric acid; the whole of the air must be expelled from the platinum and glass tubes by a stream of carbonic anhydride before sealing the glass tube, otherwise a considerable quantity of platinum is dissolved by the acid, and even when the air is expelled, the solution obtained contains about 0·5 per cent. of this metal, which has to be removed by precipitation with hydrogen sulphide after separating the silica. Two analyses of a sample of labradorite were made; the results agree well with those obtained by the usual methods. F. S. K.

Estimation of Inorganic Salts in Small Quantities of Blood. By G. N. STEWART (*Proc. Physiol. Soc.*, 1890, 18—21).—The method depends on the fact that the blood, so far as its electrical resistance is concerned, is practically a dilute solution of the inorganic salts in it. In dilute solutions of a single electrolyte, the resistance is inversely proportional to the strength of the solution. If the total amount of ash varies, and the relative proportions of the different salts do not vary, then it would be sufficiently accurate for the purpose to determine the ash by incineration once for all, and to measure the resistance of a standard tube of the same blood. The relation between resistance and ash would then enable one to calculate the latter from the former in any other case. Even if considerable variations in the relative proportions of the different salts occur, the resistance is found to correspond very fairly with the amount of inorganic material. Thick-walled glass tubes of uniform and fine internal calibre were used. The fine column of blood in these was, by non-polarisable electrodes, connected with a galvanometer, or by platinum wires to an electrometer. W. D. H.

Estimation of Zinc and Nitrogen in Pickled Railway Sleepers. By A. GRITTNER (*Zeit. ang. Chem.*, 1890, 386—387).—For estimating the zinc, the wood may be incinerated alone in a platinum basin at a dull-red heat, over a bunsen burner, or more rapidly by mixing 10 grams of fine raspings with 5 grams of sodium carbonate and 2 or 3 of potassium nitrate, and cautiously burning in a platinum basin. The charred mass is treated with acetic acid, the undissolved matter with the filter returned to the basin, and completely incinerated. The ash is dissolved in acetic acid, and the solution filtered into the former solution. The solution is mixed with a little sodium acetate, and precipitated by hydrogen sulphide. After 12 hours, the precipitate is collected on a close-grained filter, washed with water containing hydrogen sulphide and a little acetic acid, and weighed as usual. Test analyses showed a very satisfactory approximation.

The nitrogen in wood is best estimated by Kjeldahl's method. The following results show considerably less nitrogen than found by either Chevandier or Weber :—

	Summer wood.	Winter wood.
Pine, 25 years old	0·160	0·185
Beech, 130 years old	0·189	0·176
Oak, 120 years old	—	0·179

The steaming to which wood is subjected before impregnating with preservatives reduces the nitrogen by about one-fifth.

M. J. S.

Detection of Traces of Copper in Distilled Water. By H. THOMS (*J. Pharm.* [5], **23**, 27—29; from *Pharm. Centralhalle*, 1890; after *Mon. Sci.*, 1880).—Copper to the extent of 1 : 200,000 in distilled water gave no indication with either ammonia or potassium ferrocyanide, but with potassium iodide solution, a faint yellow colour appeared which gave a distinct blue tint with starch paste. A comparative test with pure distilled water showed no coloration with iodide. J. T.

Volumetric Estimation of Cobalt. By M. A. v. REIS and F. WIGGERT (*Zeit. ang. Chem.*, 1890, 695—696).—In presence of an excess of zinc oxide, cobaltous salts are oxidised to cobaltic oxide by permanganate, but the end of the reaction cannot be observed since the precipitate refuses to subside. On adding an excess of permanganate, however, and titrating back with a reducing agent, the precipitate settles well and the colour of the liquid is easily seen. The values of the solutions must be ascertained empirically, as the reactions do not correspond precisely with the equations. The best results have been obtained by the following mode of procedure:—The cobalt solution is freed from sulphates by barium nitrate, and then from excess of acid either by evaporation or by neutralising with soda. The liquid is diluted to 300 c.c., mixed with a small excess of zinc oxide, and heated to boiling. An excess (5—10 c.c.) of standard permanganate is run in and the boiling continued for 10 minutes. 30 c.c. of zinc chloride solution (made by neutralising a 19 per cent. hydrochloric acid with zinc oxide) is added, and the excess of permanganate titrated back by arsenious acid. The results are fairly satisfactory, but the method is, perhaps, capable of improvement. M. J. S.

Elementary Analysis by an Electrothermal Method. By J. OSER (*Monatsh.*, **11**, 486—500).—The substance to be burnt is placed in a porcelain boat surrounded by a coil of platinum wire, which is contained in an ordinary combustion tube. A stream of oxygen is passed along the tube, and at the same time the platinum wire is heated to redness by means of an electric current, the wires being kept insulated by passing through narrow apertures in a porcelain cylinder fitting into the tube. In order to insure perfect combustion, the decomposition products and the excess of oxygen are led through a narrow aperture in the porcelain cylinder filled with granular copper oxide and heated to a high temperature by an electrically ignited platinum wire which also passes through the canal. The author gives details of the precautions necessary to ensure satisfactory results by the method, and accompanies his description with the numerical results he has obtained, and a sketch of the apparatus employed. The ultimate object is to effect in one apparatus the elementary analysis and the determination of the heat of combustion of the substance. The description of the manner in which the latter is to be simultaneously effected is reserved for a later communication. G. T. M.

New Potash Apparatus for Use in Elementary Analyses. By A. DELISLE (*Ber.*, **24**, 271—273).—The new apparatus, a diagram of which is given, consists essentially of a small glass cylinder containing potash, and provided with a bulbed inlet tube and an inverted U-shaped outlet. The stem of the inlet tube is fused into the top of the cylinder, and passes to within a short distance of the bottom of the vessel; attached to this tube, and a short distance apart, are two discs (made by blowing bulbs on the inlet tube and then compressing them) slanting slightly downwards so as to form conical partitions which do not quite reach to the circumference of the cylinder. When the apparatus is in use, air collects under the discs and the potash becomes separated into three layers by two air chambers, so that the gas passes through the liquid three times. The exit is an inverted

U-shaped removable tube, one end of which is ground into the cylindrical vessel, the other being drawn out to a smaller diameter; one half of this tube is filled with solid potash, the other with calcium chloride or soda-lime.

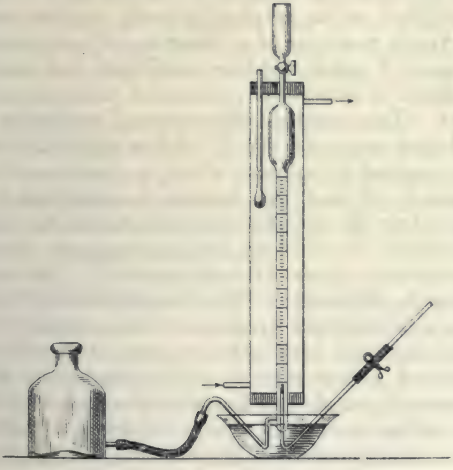
The apparatus is easily filled and emptied and its weight when filled for use is about 65 grams. F. S. K.

Estimation of the Inorganic Constituents of Soils. By Berthelot and G. André (*Compt. rend.*, **112**, 117—121).—The authors emphasise their previous statements (Abstr., 1888, 120, 384, 743) that accurate analyses of soils cannot be made by mere treatment with acids, even after calcination. For estimations of alkalis, iron, and aluminium, an elimination of the silica is always necessary, and this is true also in many cases for the estimation of calcium and magnesium. No accurate or useful distinction can be made between silicates that are attacked by acids and those that are not attacked. The organic acids in plant-roots decompose silicates, and utilise their constituents, even though the same silicates offer considerable resistance to the action of inorganic acids. C. H. B.

Estimation of Fusel Oil in Spirits. By A. Stutzer and O. Reitmair (*Zeit. ang. Chem.*, 1890, 522—531).—The authors have sought to modify Röse's process (Abstr., 1885, 600) so as to make it capable of estimating smaller proportions of fusel oil. The influence of temperature variations was eliminated by making all the readings at as near 15° as possible, and applying a correction of $\pm$ 0·01 c.c. for $\mp$ 0·1°. With regard to the pure alcohol required to furnish a datum line for the increments in the volume of the chloroform, it was found that when specimens, purchased as "*purissimum*," were fractionally distilled, both the early and late fractions gave higher values than the intermediate ones. A large apparatus was used in which 250 c.c. of alcohol and 50 c.c. of chloroform could be shaken and in which differences of 0·01 c.c. could be estimated, corresponding with 0·0028 per cent. of amyl alcohol, but the experimental errors were assumed to amount to about four times this quantity, so that (since spirits of high alcoholic strength have to be diluted to 30 per cent. before testing) 0·06 per cent. in the original spirit is the smallest quantity that can be estimated with certainty. On distilling a spirit which did not indicate more than 0·1 per cent. of amyl alcohol, with a sufficient excess of calcined potash, 900 c.c. could be distilled from a litre without an appreciable amount of the fusel oil passing over, whilst the whole of the amyl alcohol could be obtained in the last fraction by distilling to dryness, then adding 100 c.c. of water to the residue in the retort, and distilling again. In this way, anything exceeding 0·01 volume per cent. could be detected with certainty. When more than 0·1 per cent. is present, it begins to pass over earlier, so that with 0·5 per cent. even the first $\frac{1}{3}$ of the distillate is distinctly contaminated. In examining samples of high purity, the middle fraction should be used as the standard alcohol. The earlier fractions often contain substances which give a negative result. The spirit to be tested should first be distilled with potassium hydroxide. A portion of the distillate is then accurately diluted to 30 vols. per cent. (0·9656 sp. gr. at 15°), and 250 c.c., with 2·5 c.c. of sulphuric acid of 1·286 sp. gr., shaken with 50 c.c. of chloroform. With pure alcohol, the volume of the chloroform will increase to 54·5 c.c. If more than 0·15 per cent. of fusel oil is indicated, it will be necessary to remain satisfied with the accuracy thus obtainable; if less is shown, one or more litres with 100 grams of dry potash per litre is slowly fractionated. The first half of the distillate is rejected, the remainder is collected in fractions of 100 c.c., and when distillation ceases 200—250 c.c. of water is added, and 100 c.c. more distilled by the heat of a paraffin bath. This is used to dilute the last alcoholic fraction. Each fraction is diluted to 0·9656 sp. gr. and 250 c.c. shaken with acid and chloroform as above. M. J. S.

Analysis of Dynamite. By SCHEIDING (*Zeit. ang. Chem.*, 1890, 614—615).—It is usually only necessary to estimate the nitroglycerol and the moisture. The former is extracted with ether, and weighed after evaporating the ether and drying over sulphuric acid. Warming must be avoided, since even at 40° nitroglycerol volatilises perceptibly. The mineral constituents are infusorial earth and barytes, with small quantities of sodium carbonate, chalk, or magnesium carbonate. When other substances soluble in ether are present, the nitroso-nitrogen may be estimated by means of Lunge's nitrometer, or better by the Schulze-Tiemann modification of the ferrous chloride process.

In gelatin dynamite there are both nitroglycerol and nitrocellulose, besides potassium nitrate. On treatment with ether, the nitroglycerol is removed. Water then extracts the nitrate, together with sodium carbonate and other salts: a mixture of ether and alcohol (2 : 1) then dissolves (from the re-dried substance) the lower nitrocelluloses, and finally, any trinitrocellulose may be dissolved by ethyl acetate. There may remain wood meal, chalk or magnesia, and sometimes red bole or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barytes, the last of which must be regarded as an adulterant. For collecting the nitric oxide when using Schulze's process, the author recommends the form of eudiometer here figured. The narrow tubes are fused in at the bottom. M. J. S.

Potassium Mercuro-iodide as a Reagent for Aldehydes. By L. Crismer (*J. Pharm.* [5], **23**, 29—30; from *Deuts. Chem. Zeit.*, 1889, 81; after *Mon. Sci.*, 1890).—The aldehydes give a pale-yellow to brown or black precipitate, according to the concentration, with an alkaline solution of potassium mercuro-iodide. The addition of baryta water to the solution of mercury chloride in potassium iodide is preferable to the employment of soda or potash; still Nessler's reagent serves very well. Rectified commercial ether, for example, always contains aldehyde, even that distilled over sodium. To remove this impurity, the ether is agitated with increasing quantities of the reagent until no further precipitate is produced. After decantation, the ether is dried over potassium carbonate and distilled, when it boils at 34·5° to 35°, and has a density of 0·718 at 17·5°. J. T.

Acetone in Urine. By Salkowski and T. Taniguti (*J. Pharm.* [5], **23**, 194; from *Répert. de pharm.*).—Urine is often found to contain acetone, which may be estimated by adding 10 c.c. of concentrated sulphuric acid to 300 c.c. of the urine and distilling as far as possible; to the distillate aqueous potash is added, then a solution of iodine in potassium iodide, and the mixture allowed to remain 24 hours. The iodoform is then collected, dried, and weighed. The acetone does not appear to pre-exist in the urine, but is formed by distillation with an acid, and the amount varies with the amount of acid added, and with the total amount of distillate. J. T.

Urochloralic Acid in Urine. By Wagner (*J. Pharm.* [5], **23**, 115—116°; from *Arch. Med. et Ph. milit.*).—About 20 c.c. of urine is passed through a moistened filter, half of it evaporated on the water-bath, acidified with sulphuric acid, cooled, and repeatedly agitated with fresh portions of a mixture of one volume of alcohol and two volumes of ether. After distilling, the residue saturated with a slight excess of potash is exhausted three times with boiling absolute alcohol. This solution, filtered, and perfectly limpid, is precipitated by a large excess of ether. After about 24 hours, the sides of the flask are covered by minute, white, crystalline tufts. The ether is carefully poured off, and the deposit is dissolved in cold water; after filtration, a few drops of the solution can be applied to show the reducing action of the acid on alkaline copper or bismuth solution, or on an ammoniacal silver nitrate solution. In each case, very decided reduction is obtained. This reduction may, however, be due to dextrose, so that further treatment is necessary. The alkaline liquid is slightly acidified with nitric acid, and freed from chlorides by slight excess of silver nitrate. The filtrate is boiled for two hours with excess of potash and five or six volumes of alcohol of 95°. After removing silver oxide and alcohol, nitric acid and silver nitrate give a perceptible precipitate of silver chloride, which gives the amount of the chlorine derived from the urochloralic acid in the urine. 500 c.c. of a normal urine gave negative results. J. T.

Bleaching of Beeswax; Composition of White Wax. By A. Buisine and P. Buisine (*Bull. Soc. Chim.* [3], **4**, 465—470).—In the bleaching of beeswax, light is the chief factor, since the bleaching goes on in a vacuum, or in an atmosphere of carbonic anhydride, nitrogen, &c., but ceases in the dark even in an atmosphere of ozone. Pure beeswax becomes brittle when bleached by exposure; and to prevent this, it is customary to add 3—5 per cent. of suet, which also expedites the bleaching process; the addition of turpentine oil has a similar effect. Other agents made use of are:—Potassium permanganate, potassium dichromate, hydrogen peroxide, and animal charcoal. The following table shows the alteration in chemical character suffered by the wax in the bleaching process (p. 626).

Compare this vol., p. 131. T. G. N.

Modified Fat Extraction Apparatus. By J. S. Edkins (*Studies from Physiol. Lab., Owens College*, **1**, 239—241).—The apparatus described and figured is somewhat different from Drechsel's; the ether circulates more rapidly, and there is less fear of explosion as the ether is completely condensed before reaching the upper flask, instead of filling it with a mixture of cold condensed ether and hot ether vapour. W. D. H.

Estimation of Fat in Milk. By J. Gorodetzky (*Zeit. ang. Chem.*, 1890, 418—421).—On a comparison of Röse's method (Abstr., 1888, 1135) with that known as the "sand process," in which three hours' extraction with ether was used for the latter, Röse's method gave almost invariably the higher results. The extraction was therefore prolonged to five hours, and great care was taken to avoid losses when transferring the residue to the extractor. The difference now fell from an average of 0·08 per cent. to 0·04 per cent., and on further prolonging the extraction the numbers became still closer. With poor milk, the seven hours' extraction was found insufficient, quantities such as 0·02, 0·06, and 0·07 per cent. of fat being obtained by allowing the residue, after seven hours' extraction, to soak in ether during the night.

Comparing Soxhlet's areometric method (Abstr., 1881, 656) with the others, the results agreed closely (difference 0·02 per cent.) with the sand process after three hours' extraction, but with five hours' the average difference is larger (0·05). Röse's method invariably gives a higher result than Soxhlet's, the differences lying between 0·012 and 0·21 per cent., with an average of 0·081. M. J. S.

The Oleorefractometer. By F. Jean (*Bull. Soc. Chim.* [3], **4**, 105—108). The instrument consists of a hollow prism placed in the centre of a vessel which can be filled with water, and by means of which oil introduced into the prism is heated to a definite temperature. A collimator and a telescope are attached to opposite sides of the vessel in the line of the prism, and the amount of refraction produced by the oil is measured by the deflection of the shadow of a

	Melting point.	Free acids in milligrams KHO per 1 gram wax.	Total acids in milligrams KHO per 1 gram wax.	Iodine fixed per 100 wax.	Hydrogen evolved at 0° and 760 by 1 gram wax.	Hydrocarbons per 100 wax.
Pure yellow wax	63—64°	19—21	91—95	10—11	53·5—55 c.c.	13—14
Pure wax bleached by exposure	63·5—64	20—21	93—100	6—7	54—55 c.c.	11—12
Wax containing from 3—5 per cent. suet bleached by exposure	63·5—64	21—23	105—115	6—7	53·5—57	11—12
Suet	47·5	2·75	202	36·01	52·5 c.c.	
Suet after exposure to air for 40 days	48·5	4·86	213	27·68	60·4	
Wax bleached by exposure after addition of 5 per cent. turpentine	63·5	20·2	100·4	6·78	54·9	12·39
Wax bleached by hydrogen peroxide	63·5	19·87	98·42	6 26	56·1	12·53
Wax bleached by animal charcoal	63	19·71	93·2	11·36	53·6	13·3
Wax bleached by permanganate	63·7 63·5	22·63 21·96	103 29 99·23	2·64 5 8	55·5	13·34
Wax bleached by dichromate	63·2 64·0	21·86 23·43	98·9 107·72	7·94 1·08*	51·0 53·6	13·24 11·77

* ? 7·08.

vertically-interposed shutter on an arbitrary scale placed within the telescope. An oil having the same refraction as the water being placed in the prism, the latter is heated to 22°, and the shadow is adjusted to the zero of the scale, the oil to be tested is then introduced, and the corresponding deflection is read off. Animal oils produce a deviation to the left, and vegetable oils to the right, and the deviation produced by various oils varies within wide limits, so that the detection of oils and of any falsification is rendered possible.

T. G. N.

Volumetric Estimation of Albumin in Urine. By F. Venturoli (*Chem. Centr.*, 1890, ii, 795—796; from *L'Orosi*, **13**, 255—257). —The method depends on the fact that mercuric chloride precipitates albumin from urine acidified with acetic acid, before combining with potassium iodide. The standard solution of mercuric chloride is prepared by dissolving 1 gram in 100 c.c. of water, of which 1 c.c. is equivalent to 0·0245 gram of albumin, this value being determined by estimating gravimetrically the albumin in a sample of urine, and titrating it also with the standard mercuric chloride. The method is practised thus:—To 5 c.c. of urine, 6 c.c. of a 5 per cent. solution of potassium iodide is added, together with a few drops of acetic acid. The mercuric chloride solution is then run in drop by drop until a permanent yellowish-red coloration is produced. From the number of c.c. used, 1 c.c. is deducted for that which has combined with the potassium iodide, and the difference is multiplied by the factor 0·0245. If the urine should contain any alkaloïd, the results are naturally too high.

J. W. L.

Estimation of Humus in Soil by Raulin's Process. By G. Paturel (*Ann. Agron.*, **16**, 558—571).—When a solution of manganese sulphate is heated with potassium permanganate, a black precipitate of manganese dioxide, called by Raulin "manganese bronze," is immediately produced, and the liquid becomes acid and colourless. The precipitate can be redissolved by running in standard oxalic acid to the hot liquid, and the oxalic acid used is exactly proportional to the dioxide formed. If a solution of soil humus be heated with double the necessary quantity of "manganese bronze," it is completely oxidised, and the quantity of oxygen taken from the precipitate to do this can be inferred by estimating the residual "manganese bronze" with oxalic acid. On this principle is founded the following process:—The manganese sulphate solution contains 16 grams of the pure anhydrous (calcined) salt per litre; the permanganate contains 10 grams of the salt per litre, and a decimal solution also is used, made by diluting this 10 times. Normal oxalic acid, and dilute sulphuric acid containing 150 grams of sulphuric acid per litre are required in addition. The manganese solution is titrated by heating for a moment in a flask 10 c.c. of the manganese sulphate with 10 c.c. of the permanganate; 100 c.c. of distilled water and 4 c.c. of the sulphuric acid are then added, the liquid boiled, and normal oxalic acid run in from a burette until the precipitate is just dissolved; the slight excess of oxalic acid required for this is estimated by titrating back with decimal permanganate, and deducted from the total quantity used. The relation between the solutions being thus established, a precipitate of "manganese bronze" is obtained as before, in a liquid made up of 10 c.c. each of manganese sulphate and permanganate, 100 c.c. water, and 4 c.c. dilute sulphuric acid. A measured volume of the humus solution to be estimated is added to this, the quantity taken being such as will consume the available oxygen of not more than half the "manganese bronze." The mixture is heated for eight hours on a sand-bath at a temperature near ebullition, water being added periodically to replace that evaporated. The estimation of the remaining "manganese bronze" by oxalic acid is conducted as before, the difference between the two quantities of oxalic acid being a measure of the humus. The quantities of normal oxalic acid equivalent to different weights of humus determined directly by extraction with ammonia and weighing is given by Raulin in the following table:—

Oxalic acid.		Humus.	Oxalic acid.		Humus.	Oxalic acid.		Humus.
c.c.		milligrams.	c.c.		milligrams.	c.c.		milligrams.
50	=	80	800	=	885	2500	=	2315
100		150	900		975	3000		2735
200		280	1000		1060	3500		3170
300		400	1200		1225	4000		3605
400		510	1400		1390	4500		4035
500		610	1600		1560	5000		4460
600		705	1800		1720	5500		4890
700		790	2000		1890	6000		5310
						6500		5745

The humic solution is prepared for the assay by treating 10 grams of the soil (fine earth ?) with dilute hydrochloric acid to dissolve the calcium carbonate, collecting and washing the residue, and finally syringing it into a little flask with 20—30 c.c. of water ; 20 c.c. of 10 per cent. solution of sodium hydroxide is added, and the mixture heated on the water-bath for six hours, diluted with water, filtered, and washed until the washings are colourless. The filtrate is nearly neutralised with sulphuric acid, keeping, however, the humus dissolved (the precipitation of silica is of no importance), made up to 500 c.c., and a suitable fraction removed for analysis. When the soil humus contains 46 per cent. of carbon and 5 per cent. of hydrogen (or a C : N ratio of 10 : 1), as is the case with the plots at Grignon, manured frequently with farmyard manure, the method gives exact results. In long unmanured soil, when the ratio C : N has fallen perhaps to 5 : 1 and the humus contains 40 per cent. C and 7 per cent. H, it is otherwise, Raulin's process giving 26—27 grams humus per kilo., and direct estimation 17·5 grams. J. M. H. M.

General and Physical Chemistry.

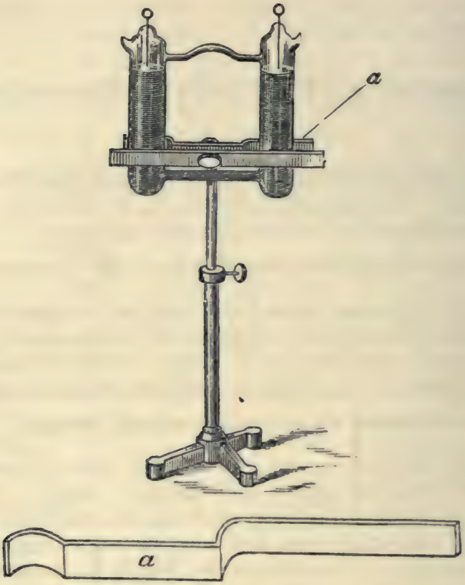
Refraction and Chemical Constitution of Gases and Vapours. By J. W. Brühl (*Zeit. physikal. Chem.*, **7**, 1—33).—In the first part of this paper, the author shows the inadequacy of the empirical expression for the molecular refraction $(n - 1)\frac{M}{d}$, as applied to gases and vapours. In passing from the liquid to the gaseous state, there is, with this formula, usually a sudden and often considerable change of value; so that relations which subsist between the molecular refraction equivalents of liquids are often lost when the substances are gasified. It is otherwise when the theoretical formula $\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{d}$, due to Lorenz and Lorentz, is employed: here there is complete optical continuity between the liquid and gaseous states. The molecular refraction is, in the vast majority of cases, the same for both states of aggregation of the substance, and may be approximately calculated from its composition. The exceptions which do occur are considered by the author to be due to the insufficient accuracy of the measurements. He is, therefore, of opinion that the empirical formula should be dropped in all comparative optical chemical investigations, and the newer theoretical formula be substituted for it.

A very complete table of the refractive indices and constants of gases and vapours is given. From the material here collected, the author concludes that the molecular refraction of gaseous substances is only very roughly an additive property, the influence of constitution being at all times very great; indeed, it is only in compounds of similar constitution that the law of simple summation holds good, and even then it is only approximate. J. W.

Refractive Indices of Water. By J. W. Brühl (*Ber.*, **24**, 644—649).—Up to the present, no measurements of the refractive indices of water for the hydrogen line H_δ and for potassium light have been made. The line H_δ, $\lambda = 4101$, is nearly coincident with the violet potassium line, $\lambda = 4044$, so that measurement for the former renders that for the latter unnecessary.

The hydrogen spectrum is obtained by means of the U-shaped induction tube shown in the sketch (next page), a strong current being required to give lines of the necessary intensity. The tube is held in a stand which is constructed so that it can be made to hold tubes of different sizes by means of the clamp *a*.

The violet potassium line cannot be obtained of sufficient intensity to serve for measurement, but the line in the red, $\lambda = 7700$, can be obtained of intensity sufficient for this purpose by heating a mixture of potassium perchlorate and chloride in the Bunsen flame. Such a mixture, prepared by heating potassium chlorate in a platinum dish



until the first period of gas evolution is at an end, is particularly suitable for the object in view, as it is readily volatile and gives a very distinct spectrum.

The results obtained are given in the following table, in which the first column contains the temperatures at which the measurements were made.

t.	K.	Li.	Hα.	Na.	Tl.	Hβ.	Hγ	Hδ.
19·9°	1·32888	1·33088	1·33120	1·33305	1·33493	1·33720	1·34045	1·34239
23·7	1·32881	1·33077	1·33091	1·33280	1·33468	1·33692	1·34016	—
25·3	1·32852	1·33041	—	1·33249	1·33447	—	—	—
26·0	—	—	1·33050	—	—	1·33625	—	—
27·0	1 32830	1·33033	—	—	1·33428	—	—	—

The results for the lithium, sodium, thallium, and hydrogen lines α, β, and γ are added for the sake of comparison, and for testing the general accuracy of the method. They agree very closely with those obtained by other observers. The above results are, therefore, most probably correct to the fourth decimal place. The water used had been repeatedly distilled (finally with potassium permanganate), and was always boiled before every new determination. H. C.

Relations between the Spectrometrical Constants and Chemical Constitution of Epichlorhydrin, of Acetaldehyde and Paracetaldehyde, and of Benzene. By J. W. Brühl (*Ber.*,

24, 656—668).—In a previous paper (this vol., p. 633), the author shows that a study of the heats of combustion is not sufficient for the determination of the chemical constitution of many organic compounds. This advantage he claims, however, to a much larger degree on behalf of the spectrometrical constants, the molecular refraction and dispersion. He discusses the case of acetaldehyde and paracetaldehyde, and that of epichlorhydrin, showing that the formulæ assigned to these compounds on purely chemical evidence are also those which would be derived from the molecular refraction and dispersion. The latter case is of particular interest on account of the relation between epichlorhydrin and the alkylene oxides. According to their thermochemical behaviour, the alkylene oxides would have to be classed as unsaturated compounds, but the spectrometrical measurements support the usually accepted formulæ for these substances, which represent them as saturated compounds. These results are, however, as already pointed out, not perfectly in accordance with the fact that the alkylene oxides readily form additive products and undergo polymerisation.

But the author holds that the power of forming additive products or undergoing polymerisation is not solely due to multiple linkage in the molecule, but to certain internal conditions in the molecule itself, and the state of tension existing between its various parts. It is this state of tension which chiefly determines the amount of heat developed when the molecule undergoes disintegration, and hence it may happen that saturated and unsaturated compounds, in which the tensions between different parts of the molecule are the same, will have also the same heats of combustion. The spectrometrical constants, on the other hand, depend chiefly on structural differences, and hence, unlike the heats of combustion, give real aid in ascertaining chemical constitution.

Further instances of the above are offered by the cases of trimethylene and benzene. The heat of combustion of trimethylene would lead to a formula for this compound similar to that of propylene, but this must be only taken as representing that a similar state of tension exists in the molecule of each, which may be caused by totally different peculiarities in the two cases. That this is so, is supported by the molecular refractions of the two compounds, which are very different, that of propylene indicating the presence, and that of trimethylene the absence, of a double linkage. Benzene furnishes another well-known instance, the molecular refraction pointing to the presence of three double linkages, and supporting Kekulé's formula, or assuming double and centric linkages to be equivalent, the centric formula proposed by Baeyer. H. C.

Basicity of Acids deduced from their Conductivity: Monobasic and Bibasic Acids. By D. BERTHELOT (*Compt. rend.*, **112**, 287—289).—The addition of excess of acid to solutions of normal salts of monobasic organic acids containing one-hundredth of a gram-molecule per litre, gives a conductivity agreeing with that calculated on the assumption that no chemical change takes place. In the case of formic acid alone is there a reduction below the calculated value.

It follows that acid salts of the monobasic acids do not exist in solution at the degree of dilution specified. The addition of an excess of alkali gives a reduction of about 5 per cent. for the first equivalent, but the second equivalent has practically no effect.

Normal salts of bibasic acids behave differently. When excess of acid is added, the conductivity is lower than the value calculated for a simple mixture, the reduction being due to the formation of acid salts. The actual values show, however, that the acid salt undergoes considerable dissociation into normal salt and free acid.

All these results agree with the conclusions deduced from thermochemical data. C. H. B.

Conductivities of Tribasic Acids. By D. Berthelot (*Compt. rend.*, **112**, 335—337; compare preceding abstract).—The addition of excess of acid to normal salts of tribasic organic acids produces, as in the case of bibasic acids, a conductivity lower than that calculated for a mixture of normal salt and free acid, but the effect is more prolonged owing to the existence of a second acid salt. Measurements were made with tricarballylic, citric, aconitic, and mellitic acids.

If the molecluar weight of an acid is known, its basicity can be determined by adding successive equivalents of alkali, and determining the point at which reduction of conductivity below that calculated for mere mixtures ceases. It is necessary to remember that excess of alkali added to the normal salt also produces a small effect, which ceases with the first equivalent in excess when the acid is monobasic, with the second when it is bibasic, with the third when it is tribasic, and with the sixth when it is hexabasic. C. H. B.

Conductivity of Organic Acids and their Salts. By W. Ostwald (*Compt. rend.*, **112**, 388—389, and D. Berthelot, *ibid.*, 390).—A question of priority.

Specific Heat of Mercury. By E. Heilborn (*Zeit. physikal. Chem.*, **7**, 85—87).—Experimental investigations have left undecided the question whether the specific heat of mercury increases or diminishes with rise of temperature. The author attacks the point from the theoretical side, and assuming that the total heat communicated goes to perform the work of expansion, arrives at the conclusion that the specific heat must diminish as the temperature rises. The formula he gives is $C_t = C_0/V_t^{\frac{1}{3}}$, V_t being the volume at $t°$, referred to $V_0 = 1$. J. W.

Heat of Combustion and Constitution of Organic Compounds. By J. Thomsen (*Zeit. physikal. Chem.*, **7**, 55—70).—The author showed in a previous communication (Abstr., 1887, 761) that the heat of combustion of gaseous hydrocarbons of the fatty series could be expressed by means of a simple formula, in which it was assumed that the heat of combustion of hydrogen atoms was always the same, but that carbon atoms had different heats of combustion according as they were singly, doubly, or trebly linked to each other. He gave numerical thermal values for the single, double, and triple bonds, by introducing the hypothetical heat of combustion of an isolated carbon atom, which, however, vanishes in the sum, no matter what value is attributed to it. Thus the agreement of observed with calculated heats of combustion affords no proof of the correctness of the thermal value taken as the basis of the calculation, as Dieffenbach imagines (Abstr., 1890, 1206).

In this paper, the author extends the above method to the consideration of closed carbon chains, and shows in the first place that the bonds in the trimethylene ring are not ordinary fatty single bonds. He adopts Stohmann's numbers for the heat of combustion of the aromatic hydrocarbons in the solid or liquid state, and points out that whilst benzene, naphthalene, and chrysene belong to the same class of compounds, anthracene and phenanthrene are not directly comparable with these; for the difference in the heat of combustion corresponding with C_4H_2 is the same in the first group, but different in the last. With regard to benzene, he no longer contends that nine single bonds exist in the nucleus, but rather that there are six "single" and three "double" bonds; these, however, not being the same as the single and double bonds of the fatty series. The aromatic double bond has, in fact, a higher thermal value than the aromatic single bond, if the probable heat of combustion of the isolated carbon atom is taken to be 135·34 cal., as in the author's former calculations. Naphthalene contains four double bonds; anthracene, phenanthrene, and chrysene, six. The author considers it probable that the aromatic double bond is composed of two unequally strong bonds, one of which ("peripheral") is equal to the single bond, the other ("central") being somewhat weaker. "In any case, it is indubitable that the bonds in benzene and the other typical aromatic hydrocarbons cannot all have the same value." J. W.

Relations between the Heats of Combustion and Structural Formulæ of the Alkylene Oxides, Acetaldehyde and its Polymerides, Trimethylene, and Benzene. By J. W. BRÜHL (*Ber.*, **24**, 650—656).—The heat of combustion of ethylene oxide is 312·5 Cal., that of the isomeric vinyl alcohol being 308·8 Cal. (calculated), and of acetaldehyde 281·9 Cal. The heat of combustion of propylene oxide may be calculated from that of ethylene oxide, and will then be 468·5 Cal., those of its isomerides, allyl alcohol, acetone, and propaldehyde, being 464·8, 437·2, and 440·7 Cal. respectively. It will be seen that the heats of combustion of the oxides in these two cases agree with those of the unsaturated isomeric alcohols and not with those of the saturated aldehydes. Since the heats of combustion of unsaturated are always greater than those of saturated compounds, it might from this be concluded that the alkylene oxides are substances of an unsaturated nature, a view which is supported by the readiness with which these oxides form additive products and undergo polymerisation.

The author holds, however, that conclusions like the above, drawn from thermochemical data, must be taken with great reservation. In illustration of this, he cites cases in which the thermochemical is obviously out of harmony with the other general chemical behaviour. Acetaldehyde, paracetaldehyde, and metacetaldehyde differ very considerably, not only in chemical but also in physical properties, and yet the heats of combustion of these three substances are practically the same. The heat of combustion of trimethylene is approximately equal to that of propylene, and greater than that calculated for an unsaturated compound of this composition, a fact at variance with the accepted view of the constitution of trimethylene. Thomsen has endeavoured to arrive at the constitution of benzene from thermochemical considerations, but unsuccessfully, and in a recent paper (preceding abstract) comes to conclusions opposed to those which he formerly held. These facts serve to show the difficulty in the way of at present employing thermochemical data for the discussion of chemical constitution. H. C.

Compressibility of Mixtures of Air and Hydrogen. By U. Lala (*Compt. rend.*, **112**, 426—428).—For feeble initial pressures, which may increase with the proportion of hydrogen and may rise to 1750 mm. with 49·89 per cent. of hydrogen, the compressibility of mixtures of air and hydrogen is intermediate between those of air and hydrogen separately, but diverges from Boyle's law in the same direction as the compressibility of hydrogen.

As the final pressure increases, the divergence from Boyle's law retains the same sign, but becomes greater for the mixture than for hydrogen alone, the difference increasing with the initial pressure, so that the compressibility of the mixture is always less than that of hydrogen.

As the proportion of hydrogen increases, the compressibility diverges continuously but slowly from that of hydrogen. With proportions of hydrogen between 33·08 and 39·28 per cent., however, the compressibility not only shows no further divergence from that of hydrogen alone, but tends to approach it with initial pressures lower than 1800 mm. As the proportion of hydrogen increases beyond this point, the compressibility tends to approach that of hydrogen for all the initial pressures between the limits given below, and with 49·89 per cent. the compressibility becomes intermediate between that of hydrogen and that of air, with a higher initial pressure than with any other mixtures.

The phenomena are of the same order as those observed with mixtures of carbonic anhydride and air (this vol., p. 253), but with an inverse sign.

The pressures varied between 1050 mm. and 15,600 mm., the percentages of hydrogen being 16·38, 28·12, 33·08, 39·28, and 49·89.

C. H. B.

Compressibility of Hot Water and its Solvent Action on Glass. By C. Barus (*Amer. J. Sci.* [3], **41**, 110—116).—It has been found that the compressibility of water between 0° and 63° continually decreases, but that above the latter temperature it increases. The author proposed to measure the compressibility between 100° and 300°, but found that at 185° water attacks glass so rapidly as to make measurements in glass tubes worthless.

Pressures were applied by aid of Cailletet's large force pump. The thread of water is enclosed in a capillary tube, between two end threads of mercury, and the distance apart of the two inner menisci, corresponding with any given temperature and pressure, measured by a cathetometer. The tube, suitably closed above, is exposed in a vapour-bath. At 185°, the thread of water soon loses its transparency, becoming white and cloudy. After the action has continued for about an hour, the column is solid at high pressures (300 atmos.), although it is probably only partially so at 20 atmos. In consequence of this, threads of mercury break off during advance and retrogression of the column. Further measurement is, therefore, not feasible. The glass was common lead glass, and distilled water was used.

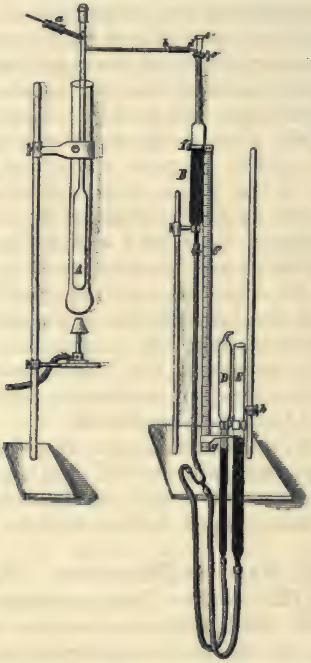
The dissolution of the glass in the water at 185° causes a shrinkage in the volume of the system of pure water and solid glass of more than 11 per cent. up to the point of solidification. The hot, turbid column, after exposure at 185° for about 55 minutes, is absolutely shorter than the original clear, cold column at 24°. The hot compressibility, after 55 minutes, has increased to five times the cold compressibility, and to three times the original hot compressibility. Making allowance for the shrinkage due to chemical action, the normal compressibility of pure water at 185° is estimated as not greater than $70/10^6$. Above 100°, therefore, the compressibility increases at a very low rate with temperature, which the author thinks indicates exceptional stability of the water molecule.

The author regards the action above described as due to the instability of the glass molecule at 185°, and as a general deduction infers that in many instances a definite dissociation temperature of the solid must first be surpassed, before solution will set in.

H. C.

Determination of Vapour Densities. By G. Lunge and O. Neuberg (*Ber.*, **24**, 729—737).—The gasvolumeter devised by one of the authors (Abstr., 1890, 660) may be used in conjunction with V. Meyer's apparatus for the determination of vapour densities, and, since the reduction of the volume of gas measured to standard conditions is thus rendered unnecessary, a great saving of time is effected. It has, however, an additional advantage, for with but slight alteration in the apparatus itself, it becomes possible to effect the volatilisation of a compound under greatly diminished pressure with the greatest ease. A sketch is here given of the apparatus so arranged as to effect the above object.

The vapour density apparatus *A*, the bulb of which should have a capacity of from 300 to 400 c.c., is fitted with the arrangement *a*, formerly described by Meyer and Biltz (Abstr., 1888, 1241) for allowing the substance under examination to fall into the bulb at any desired moment. *a* is in this case placed above the capillary tube *b*, and the latter, in place of being bent downwards, is kept horizontal and brought close up to the tube *d* of the measuring vessel *B*, the two being then connected by stout india-rubber tubing. The measuring tube *B* consists of a narrow upper and wide lower portion, the upper portion, which contains 15 or 16 c.c., being divided either into one-tenth c.c., or into divisions of 0·774 c.c., each of which corresponds with 1 milligram of dry air at 0° and 760 mm., these being again subdivided into tenths. By means of the tap *c*, *B* may be placed in communication with *d* and *b* and thus with *A*, or may be connected with the small vessel *e*, and thus with the outside air. A wooden scale, *C*, 80 cm. long, and divided into millimeters, is fastened by means of the clamp *f* to the lower, wider portion of *B*. A moveable index needle, *g*, is placed on the scale *C*, and can be held in any position of the scale by means of a spring. The rest of the apparatus consists of the reduction tube *D* and the pressure tube *E*, the functions of which were described in the former paper.



If *B* and *e* are placed in communication and *E* be then raised, the air will be driven out of *B* and the mercury will rise until it reaches the tap *c*. By closing *c* and lowering *E* until the mercury in *B* falls to the clamp *f*, which marks the zero of the scale, and then adjusting *g* to the level of the mercury in E, it is obvious that the reading on the scale of the position of *g* will be the barometric pressure at the time of the observation. From this is subtracted the pressure at which the vapour density is to be taken, and *g* is then adjusted in the position so found. For instance, if the height of the barometer is 750 mm., and the pressure at which the experiment is to be conducted is 50 mm., *g* would be adjusted at division 700 on the scale.

In conducting an experiment, *B* is first connected with *e*, *E* is raised, and the air driven out of *B*. *c* is now turned so as to put *d* and *B* into communication, and *E* is lowered as far as possible. *c* is then again turned and the gas which has entered *B* is driven out by raising *E*. The above operations are then repeated for a number of times, until the desired pressure within the apparatus is reached. This can be done while *A* is being heated to the necessary temperature. The mercury in *B* is now adjusted so that it fills the whole tube to the tap *c*, which is then so turned as to put *B* and *A* into communication. When this is done, the substance, the vapour density of which is being determined, is allowed to fall into the bulb *A*. Volatilisation immediately sets in, and the mercury in *B* sinks, whilst at the same time it rises in *E*, but by lowering *E* it is possible to maintain the pressure within the apparatus practically constant while the gas is coming off.

When the evolution of gas ceases, *c* is turned so that communication with both *A* and *e* is cut off, *b* and *d* are disconnected, and the tube *B* is lowered to a height convenient for reading. The reduction tube *D*, which up to this time is neglected, is now raised so that the level of the mercury in this tube and *B* shall be about the same, and a sufficient time is allowed for the temperature in both tubes to become equal. *E* is then raised until the mercury in *D* stands at the mark 100, when the air in *D* is compressed to the volume occupied at 0° and 760 mm. At the same time, the level of the mercury in *D* is brought to that in the tube *B*, so that the gas in the latter tube is also under the conditions 0° and 760 mm. If *B* is divided into cubic centimeters, the desired vapour density will be g/v 0·001293, when g is weight of the substance in grams and v is the volume of the gas in *B*. If the divisions on *B* are each 0·774 c.c., corresponding with 1 milligram of air, the above formula will be simplified to g/v_1, where g is the weight in milligrams and v_1 the volume measured.

The air in *A* may, of course, be replaced by any other indifferent gas, preferably not by hydrogen, before the exhaustion is commenced. In the following table is given the reduction in the boiling point which substances, boiling under ordinary pressure at the temperatures at the head of each column, will approximately undergo when the pressure is reduced to that given in the table :—

Ordinary boiling point ..	below 100°			100—200°			200—300°			above 300°		
Pressure in mm..	20	50	75	20	50	75	20	50	75	20	50	75
Reduction in boiling point..............	65°	55°	50°	80°	65°	60°	105°	90°	80°	130°	100°	90°

It is, however, best to heat the bulb *A* to about 20° above the point at which the substance boils under the pressure of the experiment.

A number of examples are given to illustrate the accuracy of the above method of determining vapour densities. It is proposed to employ it for the investigation of certain doubtful cases, such as those of ammonium chloride and sulphur. H. C.

Kinetic Molecular Theory of Dilute Solutions. By H. A. Lorentz (*Zeit. physikal. Chem.*, **7**, 36—54).—Like Boltzmann (this vol., p. 389), the author endeavours to deduce the law of osmotic pressure from the molecular motions in dilute solutions. He also treats of the freezing point and vapour pressure of such solutions from the same standpoint, and finds the theory of electrolytic dissociation in harmony with his conclusions. J. W.

Osmotic Pressure and the Kinetic Theory of Gases. By L. BOLTZMANN (*Zeit. physikal. Chem.*, **7**, 88—90).—Lorentz (preceding abstract) raised an objection to a mode of proof adopted by the author in his paper (this vol., p. 389). The validity of the objection is admitted, and a stricter proof given. J. W.

Dissociation Hypothesis. By J. TRAUBE (*Ber.*, **24**, 737—745).—A reply to Arrhenius (this vol., p. 521). The author does not regard the answers given by Arrhenius to the objections he brought forward against the dissociation hypothesis (this vol., p. 255) as satisfactory, and in this paper repeats and extends these objections. H. C.

Affinity of Bases. By E. LELLMANN and H. GROSS (*Annalen*, **260**, 269—289; compare Abstr., 1889, 1104).—The authors have measured the affinity of various bases by the spectrophotometric method previously described by Lellmann (*loc. cit.*).

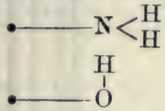
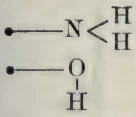
A dilute alcoholic solution (50 c.c.) of dimethylamidoazobenzene (butter-yellow), containing 2 milligrams of the base, is mixed with a known quantity of the hydrochloride of the base to be investigated, and the mixture made up to 100 c.c. This mixture attains a condition of equilibrium after a longer or shorter time (sometimes immediately, sometimes only after four to five days) on keeping at the ordinary temperature, but the distribution of the acid takes place more quickly on heating at 40° for one to two hours. The solution is then examined with a spectrophotometer, and its absorption compared with that of a solution of pure dimethylamidoazobenzene hydrochloride in a large excess of hydrochloric acid.

In the case of aniline, it was found, as the average of four different experiments, that equilibrium is attained when the number of molecules of hydrochloric acid combined with the dimethylamidoazobenzene, compared with the number of molecules of acid in combination with the aniline, is 1545 : 100,000, or $\kappa = 0{\cdot}01545$, the acid and the two bases being present in the proportion of their molecular weights. When such solutions are kept for some days longer and examined again, the value of κ is found to have undergone a slight change in every case, but the variations are such that the average value remains practically the same. A similar variation is observed in the case of other bases, a fact which shows that the solutions are not actually in a state of rest; it may be noted that those solutions which at the first examination give a value for κ considerably above the average, on examination at a later period, give a value considerably below the average, and *vice versâ*, whilst those which give values approximately the same as the average do so also at the later period.

The bases given in the following list were investigated; they are placed in the order of their affinity, commencing with the feeblest, and the figures give the value of κ.

Parachloraniline....	0·03595	Dimethylaniline....	0·01003
Metamidophenol....	0·02138	Paratoluidine......	0·00990
Quinoline..........	0·02055	Quinaldine........	0·009297
Orthotoluidine.....	0·01818	Paramidophenol....	0·006856
Aniline............	0·01565	α-Picoline.........	0·005838
Orthamidophenol...	0·01444	Hydroxylamine....	0·004715
Pyridine..........	0·01323	Ammonia..........	0·0003066

The results arrived at by the spectrophotometric method differ very considerably from those obtained by Walker by measurements of the electrical conductivity (*Zeit. physikal. Chem.*, **4**, 319); experiments showed that this difference is not due to the fact that in one case dilute alcoholic, and in the other aqueous, solutions are employed. In the authors' opinion, Walker's series is probably incorrect, for various reasons.

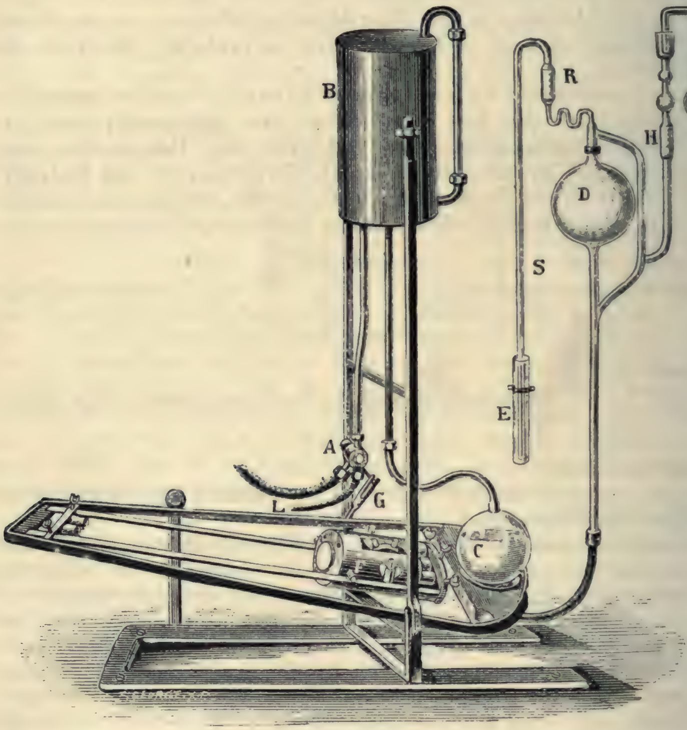
The article continues with an attempt to explain various anomalies in the above list; the fact that ortho- and par-amidophenol are stronger, whilst metamidophenol is a weaker, base than aniline, may be accounted for by assuming that the hydrogen of the hydroxyl group is nearer to the amido-group in the ortho- and para-compounds than it is in the meta-derivative; in the first case, the atoms may be supposed to be arranged thus,  ; and in the second case thus,  ; the influence of the hydroxy-group being different in the two cases.

Numerous remarkable facts observed by Ostwald may be explained by a hypothesis of this kind.

Experiments seem to show that dimethylamidoazobenzene and other coal-tar colouring matters may be employed for studying various other phenomena; it has been found, for example, that of the three liquids, methyl alcohol, water, and ethyl alcohol, the first has the smallest, the last the greatest attraction for hydrochloric acid, and this in solutions so dilute that a chemical reaction must be considered out of the question. F. S. K.

Velocity of Reaction in Gelatin. By S. REFORMATSKY (*Zeit. physikal. Chem.*, **7**, 34—35).—Parallel experiments on the catalysis of methyl acetate by hydrochloric acid were instituted in water and in agar-agar jelly. The concentration of the agar-agar solution (1·25 per cent.) was chosen so that at 35° it was liquid, but at 25°, the temperature of experiment, solid enough to allow the vessel in which it was contained to be inverted without any trace of fluid escaping. The coefficient of velocity was found to be the same in both cases, as was to be expected, considering the identical results obtained by Voigtländer (Abstr., 1889, 817) for diffusion in such a jelly and in pure water. J. W.

New Automatic Mercury Air-pump, with Arrangement for Self-action by means of Water Pressure. By M. Stuhl (*Ber.*, **24**, 147—159).—A great disadvantage attending the use of the mercury air-pump is the necessity of constantly raising the mercury back to its former level, in order to keep the pump in action. This usually employs the whole time and attention of the operator, and often gives rise to accidents of all kinds. In order to overcome this difficulty as far as possible, the author has devised a method of keeping the pump automatically in constant action by means of water pressure. The arrangement used is illustrated by the accompanying sketch.



Water enters through the tube L, and three-way tap A, into the cylinder B, the air escaping into the glass vessel C, and by its pressure forcing the mercury into the pump D, and effecting exhaustion in the well-known manner. The long barometer tube is replaced by the glass valve H.

As soon as a sufficient amount of mercury has been pressed into the pump, the beam on which the vessel C is supported becomes heaviest on the left-hand side, and is depressed in this direction; this causes a rotation of the three-way tap in such a manner that the water supply is shut off, and the water which is under the pressure of the air is removed by the tube A. At the same time, the moveable weight F also falls to the left hand, and serves so to increase the weight on this side that the whole of the mercury must flow from D into C, before the latter becomes the heavier; then rotation of the beam and tap again take place, the weight F falls to the right, and the pump is once more set in action.

To the moveable weight F is attached an arrangement by means of which the air collecting in the globe D can be transferred for five successive times into a small and perfectly vacuous receiver, R, and not until the sixth time of working the pump allowed to escape into the air. This is effected by attaching to the weight F a small, six-toothed wheel, having a deep incision between two of the teeth. Each time the weight falls to the right the wheel is rotated through the distance between two of its teeth, and a peg, which serves to stop the falling weight, comes for five successive times in contact with the circumference of the wheel. The sixth time, however, the peg enters the incision, and the weight thus falls further to the right. This time, therefore, a larger quantity of mercury must be forced out of C into D before the beam is over-balanced on the left-hand side, and this can be so arranged that the mercury now fills the whole of the small receiver R, and forces the air contained in it through the tube S into the atmosphere. In this way, very perfect exhaustion can be effected.

The above arrangement in connection with the weight F renders it possible to regulate the height to which the mercury will rise to within half a centimeter. The rate at which the mercury rises can very easily be regulated by means of the tap. Instead of allowing the air to escape directly into the atmosphere, it may first be passed into a second receiver, which is exhausted by means of a water-pump. The most perfect exhaustion is thus obtained. H. C.

Inorganic Chemistry.

Conversion of Sodium Pyrophosphite into Sodium Hydrogen Phosphite. By L. Amat (*Compt. rend.*, **112**, 527—530).—The conversion of sodium pyrophosphite in aqueous solution into sodium hydrogen phosphite follows the same law as the hydration of metaphosphoric acid (Abstr., 1889, 671), the equation being $\log \frac{l - \phi_0}{l - \phi} = kx \log e$; where ϕ_0 is the quantity of acid phosphite originally present, ϕ the quantity present at any given instant, l the maximum possible quantity of acid phosphite, and x the time in hours.

The change is more rapid the more concentrated the solution, but the velocity of transformation is such that k remains constant, the decrease in velocity owing to reduction being compensated by the accelerating influence of the acid phosphite.

In presence of free acid (sulphuric), the rate of change is greatly increased, doubtless because the acid liberates pyrophosphorous acid, which rapidly alters. Under these conditions, the value of k gradually decreases, and the equation already given only represents the results in a very general way. C. H. B.

Silicobromoform. By A. Besson (*Compt. rend.*, **112**, 530—532).—When carefully dried hydrogen bromide acts on crystallised silicon at a temperature below redness, the product consists of silicon bromide boiling at 153° and silicobromoform, in proportion which, even under favourable conditions, does not exceed 5 per cent. of the product. When air is allowed to enter the apparatus, a substance is formed which crystallises in yellow plates; it seems to be a silicon oxybromide.

Silicobromoform is a colourless liquid which does not solidify even at $-60°$, and boils without decomposition at 109—111° in presence of an inert gas. In presence of air, it fumes abundantly and ignites spontaneously; its vapour forms explosive mixtures with air. It is decomposed by water, and also, with great violence, by alkalis.

Ammonia acts energetically on silicobromoform with development of heat and light, but the white product is indefinite in composition, and contains silicon, hydrogen, bromine, and ammonia. Hydrogen phosphide does not combine with silicobromoform at $-40°$ under ordinary pressure, but under a pressure of 25 atmos. at $+15°$, a white solid is formed, which persists for some time after the removal of the pressure. Silicochloroform yields a similar product, which, however, decomposes as soon as the pressure is removed, even at $-22°$.

C. H. B.

Sodamide and Disodammonium Chloride. By Joannis (*Compt. rend.*, **112**, 392—394).—Sodammonium decomposes very slowly at the ordinary temperature into hydrogen and sodamide, the change being slightly more rapid when exposed to light than in the dark. The decomposition tends to a limit as the pressure of the hydrogen increases. As the hydrogen and excess of ammonia escape, the sodamide, NH_2Na, separates in white, transparent crystals, about 1 mm. long.

Sodium chloride interacts with sodammonium, but does not form the subchloride described by Rose. One equivalent of hydrogen is liberated for each equivalent of sodammonium used, and when the sodium chloride is in excess, the liquid becomes colourless. The precipitate, when washed with liquefied ammonia, is sodamide free from chlorine. The rapid decomposition of sodammonium under these conditions is due to the formation of an unstable disodammonium chloride, NH_2Na_2Cl, which can be obtained (mixed with excess of sodium chloride) by the action of excess of sodium chloride on sodium in presence of a quantity of liquefied ammonia insufficient to dissolve all the sodium chloride. It is decomposed by liquefied ammonia into sodium chloride and sodamide, and is also decomposed by water, without noise and without evolution of hydrogen, yielding ammonia, sodium hydroxide, and sodium chloride. C. H. B.

Combination of Ammonia with Chlorides. By JOANNIS (*Compt. rend.*, **112**, 337—339).—Fused sodium chloride dissolves readily in liquefied ammonia at −10°, the vapour pressure of the solution being slightly inferior to that of the liquefied gas alone at this temperature. On further cooling to −30°, and allowing the ammonia to escape at ordinary pressure, slender, white needles quickly separate. After evolution of gas at −30° has ceased, the temperature is allowed to rise slowly. Very little gas escapes up to −24°, but beyond this point the evolution of ammonia becomes more rapid. The gas evolved above −24° was collected in dilute acid; it was found that the ratio $NH_3/NaCl = 4·998$, and hence a compound is formed of the composition $NaCl,5NH_3$. It has the following dissociation pressures:—

−24°	−20·8°	−17·5°	−15·0°	−10·0°	−7·0°
777	892	1074	1305	1777	2130 mm.

No evidence could be obtained of the formation, even at −72°, of any compound of potassium chloride and ammonia recognisable by a specific tension of dissociation.

Barium chloride combines very slowly with ammonia, but if the anhydrous salt is brought in contact with the liquefied gas, combination takes place somewhat rapidly, and if the excess of ammonia is allowed to escape at 0° under atmospheric pressure, the residue has the composition $BaCl_2,8NH_3$. Its dissociation pressure is 541 mm. at 0° and 1850 mm. at 28·4°, and if the ammonia is continually removed, the pressure remains constant at the latter temperature until decomposition is complete. C. H. B.

Dissociation of Magnesium Oxide by Means of Metallic Magnesium. By H. N. MORSE and J. WHITE (*Amer. Chem. J.*, **13**, 128—129).—The authors have already described the dissociation of the oxides and sulphides of zinc and cadmium when heated in a vacuum with their respective metals (Abstr., 1889, 755). The method employed for similar experiments on magnesium oxide was the same, except that an iron tube, closed at one end, was inserted into the back half of the glass tube to prevent contact of the magnesium vapour with the glass. The magnesium was distilled in a vacuum as described by Burton and Vorce (Abstr., 1890, 850), and the oxide was heated to redness in a vacuum until it ceased to give off carbonic anhydride; from 4·5 to 10 grams of the metal was then dropped into the tube, followed by 1·5—3 grams of the oxide. The tube was exhausted and heated to bright redness, when the phenomena that presented themselves were similar to those observed in the previous experiments, the magnesium oxide being transported to the front part of the tube, in quantity varying with the thoroughness with which the metal and oxide were mixed. Carbonic anhydride (from the carbon in the iron) and from 1·5 to 3 c.c. of oxygen were evolved during the experiment. A. G. B.

Melting Point of certain Alloys. By F. C. WELD (*Amer. Chem. J.*, **13**, 121—123).—Heycock and Neville (Proc., 1889, 41) have shown that the addition of each atom of lead to 100 atoms of tin lowers the melting point of the tin by 2·22°. The author finds that this rule only holds with quantities of lead up to 15 atoms to 100 atoms of tin, after which the melting points are not so low as they should be when calculated by the rule. The lowest melting point obtained is that of 38 atoms of lead to 100 of tin (180°).

The effects of this reduction of the melting point are not cumulative; thus, an alloy of 100 atoms of tin with 57·28 atoms of lead melts at 180°, whilst one of 100 atoms of tin with 57·26 atoms of lead and 5·89 atoms of mercury melts at 173°, not $180° - 5·89 \times 2·3° = 166·45°$.

A. G. B.

Note.—The author seems to overlook the fact that Heycock and Neville referred explicitly to the addition of "small quantities" of lead. It is well known that Raoult's method only holds for dilute solutions. [EDITORS.]

Hydrated Lead Oxide. By C. LUEDEKING (*Amer. Chem. J.*, **13**, 120—121).—Schaffner's hydrated lead oxide, $2PbO,H_2O$, is obtained in large crystals when litharge is boiled with potassium hydroxide, and the cold solution allowed to slowly absorb carbonic anhydride by exposure to air; as the potassium hydroxide becomes converted into carbonate, short, thick, well-developed, colourless, transparent, tetragonal crystals ($a : b : c = 1 : 1 : 0·824$) are deposited; they are highly refractive and brilliantly lustrous; they are alkaline, and become opaque from formation of carbonate when exposed to air, and yellow from formation of oxide when heated, but in both cases they retain the original crystalline form. A. G. B.

Copper Arsenates. By A. HIRSCH (*Chem. Centr.*, 1891, i, 15—16; from *Inaug. Diss. Halle*).—*Tetracupric arsenate*, $4CuO,As_2O_5 + H_2O$, has been already prepared by Debray, Friedel and Sarasin, and Coloriano. The author has prepared it by the action of disodium arsenate on an excess of cupric chloride in concentrated solution. It is white, very stable, and does not react with silver nitrate; with disodium arsenate, it becomes blue. It was also obtained combined with $3\frac{1}{2}$ mols. H_2O.

Tricupric arsenate is obtained by adding sodium acetate to the filtrate from the precipitation of disodium acetate with excess of cupric sulphate. It is also obtained by the action of trisilver arsenate on cupric chloride.

Several copper sodium arsenates were prepared: $2Cu_3As_2O_8 + NaH_2AsO_4 + 5H_2O$, from disodium arsenate and excess of cupric sulphate; $6Cu_3As_2O_8 + 2NaH_2AsO_4 + Na_2HAsO_4 + 13·5H_2O$, or $33·5H_2O$, or $16H_2O$, from cupric sulphate and excess of sodium arsenate. If the excess of cupric sulphate is very considerable, the compound $5CuO,2As_2O_5$ is formed. From cupric nitrate, with excess of disodium arsenate, the salts $6Cu_3As_2O_8 + 2Na_2HAsO_4 + 19H_2O$ and $4Cu_3As_2O_8 + Na_2HAsO_4 + 11H_2O$ were obtained; whilst, if the cupric nitrate is in excess, the salts $5CuO,2As_2O_5$ and $8CuO,3As_2O_5$ are formed. The following double salts were obtained by the action of cupric chloride on disodium arsenate in dilute solution: $3Cu_3As_2O_8 + 2NaCl + 13·5H_2O$ or $17·5H_2O$, $5Cu_3As_2O_8 + 3NaCl + 19H_2O$ or

$23H_2O$, and $Cu_3As_3O_8 + NaCl + 7{\cdot}5H_2O$. The two last are obtained from the former by the decomposing action of water. The chlorine is combined with the sodium in these salts, since silver nitrate reacts with them to form silver chloride without precipitating any cupric oxide, as it would do if the chlorine were in the form of cupric oxychloride.

From all these salts, if they are washed first with cold and then with hot water, the white tetracupric arsenate is obtained.

J. W. L.

Hydrated Sodium Manganites. By G. Rousseau (*Compt. rend.*, **112**, 525—527).—Potassium permanganate at 200° splits up into an alkaline manganite and manganese dioxide, and when the action of heat is prolonged, the two products interact with formation of potassium manganite and free alkali. Sodium permanganate behaves in a similar way at about 300°, the change being complete after six hours. Boiling water removes from the product a brown, amorphous substance which probably corresponds with Gorgeu's colloïdal manganese dioxide. After repeated lixiviation, the hydrated manganite $8MnO_2,Na_2O,5H_2O$ is left in black, microscopic crystals. It loses 4 mols. H_2O at 150° to 180°. and becomes anhydrous at 250°; between this point and 440°, it undergoes no further change; but at dull redness, it begins to polymerise with loss of sodium.

Sodium manganate was prepared by heating 3 grams of sodium permanganate with 4 grams of sodium hydroxide and a small quantity of water, and when the effervescence due to liberation of oxygen ceased, 5 grams of sodium chloride was added, and the heating continued. Four to five hours heating at the highest temperature of a Bunsen burner yields silky, black needles of the hydrate

$$12MnO_2,Na_2O,4H_2O,$$

which becomes anhydrous between 130° and 170°. With a higher temperature and a larger proportion of sodium chloride, rhomboïdal lamellæ of a new hydrate, $16MnO_2,Na_2O,8H_2O$, are obtained; this loses 7 mols. H_2O between 150° and 180°, and becomes anhydrous at about 250°. At a yellow heat, the product consists of black needles, $12MnO_2,Na_2O,4H_2O$, identical in appearance and composition with those obtained at about 800° by means of a Bunsen burner.

When sodium manganate is heated from 300° up to a yellow heat, the series of changes is as follows: the first product is

$$8MnO_2,Na_2O,5H_2O,$$

which above 500° polymerises, and at 800° is converted into $12MnO_2,Na_2O,4H_2O$. At about 1000°, the compound

$$16MnO_2,Na_2O,8H_2O$$

is formed, but between 1200° and 1300° it splits up into the compound, $8MnO_2,Na_2O,5H_2O$, that is formed at 300°. At a yellow heat, the hydrate $12MnO_2,Na_2O,4H_2O$ reappears, and tends to produce another cycle of the same kind.

The author has previously observed analogous variations in the condensation of the anhydrous manganites of the alkaline earths.

C. H. B.

The Carbon of Spiegeleisen. By B. RATHKE (*Annalen*, **260**, 333—337).—When a sample of semi-crystalline ferromanganese (30 grams), containing 66 per cent. of manganese, is reduced to a fine powder, covered with water, and bromine (185 grams) gradually added to the mixture with constant shaking, until no further action is observed, a slight development of heat takes place, but no gas is evolved; on adding water and distilling, a small quantity of carbon tetrabromide, which seems to contain a little carbon tetrachloride, collects in the receiver. The insoluble carbonaceous residue, after having been repeatedly boiled with hydrochloric acid, washed, and dried at 100°, is a black, granular powder (3·7 grams), similar in appearance to gunpowder. A sample of this powder was digested with hydrofluoric acid to free it from silica, washed well, dried at 110°, and analysed with the following result (in percentages):—Carbon = 49·97, hydrogen = 2·12, bromine = 21·25, chlorine = 1·47, and oxygen = 25·19; it also contains traces of iron and manganese and has a faint acid reaction. When treated with ammonia at 100°, it loses 13·8 per cent. of bromine and 0·82 per cent. of chlorine, and the residual powder retains ammonia even after having been dried at 110°. When the original carbonaceous residue is boiled with sodium carbonate (but not with sodium chloride), it loses 13·94 per cent. of bromine and 1·58 per cent. of chlorine; the undissolved substance has a neutral reaction and the following percentage composition:—Carbon = 50·71, hydrogen = 2·13, bromine = 7·41, sodium = 7·39, and oxygen = 32·36.

These results show that the carbonaceous residue obtained from ferromanganese in the manner described above has the character of an organic acid. F. S. K.

Crystalline Ferromanganese. By B. RATHKE (*Annalen*, **260**, 326—332).—Three samples of crystalline ferromanganese were analysed with the following results:—

	Carbon.	Silicon.	Iron.	Manganese.	Phosphorus.
I......	7·47	0·18	9·48	82·45	0·10
II......	7·45	0·15	16·99	75·73	0·12
III......	6·48	0·52	47·93	44·99	—

F. S. K.

Atomic Weight of Rhodium. By K. SEUBERT and K. KOBBÉ (*Annalen*, **260**, 314—325).—The atomic weight of rhodium has been determined by the method previously employed by Jörgensen (Abstr., 1883, 1060), namely, by decomposing pure chloropurpureorhodium chloride, $Rh_2(NH_3)_{10}Cl_6$, in a stream of hydrogen.

Three different samples of metal were used for the preparation of this salt. The atomic weight was found to be 102·7 (O = 15·96) as the average of ten separate determinations. F. S. K.

Mineralogical Chemistry.

Native Silver and Dioptase from French Congo. By E. JANNETTAZ (*Compt. rend.*, **112**, 446—447).—Dioptase of an emerald-green colour was found in some cases intimately mixed with quartz crystals of the usual form and chrysocolla, in others embedded in limestone. The dioptase crystals have the usual form, and a crystal cut normally to its axis shows rings with a black cross of positive sign, as in the dioptase from the Ural.

One of the specimens of calcium carbonate, crystallised in rhombohedrons, and obtained from the copper mine of Mindouli, about two leagues east of Comba, between Bonanza and Brazzaville, contained several grains of native silver, including a group of octahedra with very distinct faces. C. H. B.

Goethite, Serpentine, and Garnet from Canada. By B. J. HARRINGTON (*Jahrb. f. Min.*, 1891, i, Ref. 241—242; from *Can. Rec. Sci.*, **4**, 93—99).—*Goethite* occurs with hæmatite, limonite, proustite, pyrolusite, calcite, and barytes in veins in the lower carboniferous limestone at Clifton, Nova Scotia. Analysis yielded the following results:—

Fe_2O_3.	Mn_2O_3.	H_2O.	SiO_2.
88·92	0·14	10·20	0·32

The sp. gr. of the mineral is 4·217, and its hardness 5.

Serpentine.—Narrow veins of white or apple-green serpentine occur in a dark serpentine in the asbestos mine at Coleraine, Eastern Townships. Fresh from the mine, the mineral is so soft that it can be moulded with the fingers. In the air, it becomes gradually harder, until it attains a hardness of 3·5. An analysis of dry material gave:—

SiO_2.	MgO.	FeO.	MnO.	NiO.	CaO.	H_2O.
43·13	42·05	0·37	trace	trace	trace	13·88

The sp. gr. of the mineral is 2·514.

Garnet is met with at Oxford, St. Jerome, and Grenville, and also in Ottawa Co., Ontario, in the well-known apatite region. Analysis yielded:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	Ignition.	Total.
36·22	18 23	7·17	0·63	37·39	0·70	100·34

B. H. B.

Manganese Ores of Transcaucasia. By N. KOZOVSKI (*Zeit. Kryst. Min.*, **18**, 630, from the *Russ. Min. J.*, **4**, 1—29).—The manganese ore, pyrolusite, occurs in a calcareous sandstone, and gave on analysis the following results:—

	H_2O.	Insol. in acids.	SiO_2.	P_2O_5.	Mn.	P.
I.	0·61	0·47	0·89	1·12	57·02	0·48
II.	1·04	5·04	4·36	1·02	55·00	0·45
III.	5·78	8·47	7·38	1·16	45·50	0·48

B. H. B.

Manganese Ore in Ekaterinoslav. By N. Kozovski (*Zeit. Kryst. Min.*, **18**, 631, from the Russian).—The ore, pyrolusite, occurs in a manganiferous clay, and gave on analysis the following results:—

	MnO_2.	P.	Fe_2O_3.	SiO_2.	CuO.	S.	MgO.	Total.
I.	85·07	trace	1·23	8·10	1·37	0·08	1·08	96·93
II.	81·03	0·36	1·90	9·33	1·95	0·07	0·85	96·43

B. H. B.

Breunerite and Bloedite, from Hall, in Tyrol. By H. v. Foullon (*Zeit. Kryst. Min.*, **18**, 658—659; from *Jahrb. k. k. Geol. Reichsanst.*, **38**, 1).—With galena, breunerite occurs in anhydrite in aggregates resembling pinolite, and gave on analysis:—

FeO.	MnO.	MgO.
11·88	1·36	37·68

Bloedite of a yellow colour is met with in the rock salt, and gave on analysis:—

SO_3.	MgO.	Na_2O.	Cl.	H_2O.	Total.
46·35	12·59	17·20	0·99	23·78	100·91

B. H. B.

Melanophlogite. By G. Friedel (*Jahrb. f. Min.*, 1891, i, Ref. 201—205; from *Bull. Soc. Fran. Min.*, **13**, 356).—The author collected a series of good specimens of melanophlogite in the Solfara Giona, in Sicily, and has subjected them to careful investigation. The mineral occurs in a bed of limestone, occurring in cavities with sulphur, calcite, and celestine. The crystals are in the form of cubes or small globes composed of a large number of cubes. From the optical examination, the author concludes that melanophlogite is formed of six quadratic pyramids, the mineral affording an example of a peculiar kind of quadratic pseudo-cube and not, as Mallard suggests, of a pseudomorph. The mineral has a sp. gr. of 2·030, and gave on analysis the following results:—

SO_3.	SiO_2.
6·19	93·18

The formula is $SO_3,20SiO_2$. There is also a variable percentage of carbon, which the author regards as unessential, as the limestone in which the mineral occurs is highly bituminous. The crust, on which the melanophlogite is planted, consists of opal, and the author is of opinion that the melanophlogite has been formed by the action of sulphuric anhydride on this mineral at a temperature not exceeding 100°. On a specimen of sulphur, the author found spheroidal groups of melanophlogite crystals, the crystals being hexagonal and exhibiting the form of tridymite. This variety he terms hexagonal melanophlogite in contradistinction to the quadratic variety crystallising in pseudo-cubes. B. H. B.

Ferronatrite. By A. ARZRUNI and A. FRENZEL (*Zeit. Kryst. Min.*, **18**, 595—598).—Under the name of ferronatrite, Mackintosh (Abstr., 1890, 455) described an iron sodium sulphate occurring with other iron sulphates in Chili. As the description of this mineral did not accord with that of a similar mineral from Caracoles, Chili, Frenzel suggested for the latter the name of *gordaite*. The mineral ferronatrite was subsequently described by Genth and Penfield (this vol., 274), and from this description the authors conclude that gordaite and ferronatrite are identical. A new analysis gave :—

SO_3.	Fe_2O_3.	Na_2O.	H_2O.	Total.
50·85	17·69	20·22	11·90	100·66

Formula : $3Na_2SO_4,Fe_2S_3O_{12} + 6H_2O$. B. H. B.

Eutaxitic Glasses of the Liparites. By P. WENJUKOFF (*Jahrb. f. Min.*, 1891, i., Ref. 281—282 ; from *Trav. soc. natur. St. Pétersbourg*, **21**, 1—19).—In the island of Unga, east of Kamtchatka and in the River Marekanka, massive rocks of banded structure occur. Light and dark bands alternate. In polarised light, under the microscope, it is seen that both rocks consist essentially of spherolites of finely fibrous, radiated structure. Analysis gave the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
I.	75·36	14·21	0·13	0·84	2·72	4·78	1·09	99·13
II.	76·19	13·42	0·41	1·35	2·63	4·57	1·15	97·72
III.	72·78	14·15	0·17	0·82	2·48	4·51	4·35	99·26

I. Banded rock from the Marekanka ; II. banded rock from Unga ; III. perlite from the Marekanka. These analyses show that these rocks are chemically indentical with various liparite glasses. They therefore belong undoubtedly to the liparites, and are distinguished from obsidian and similar rocks merely by their banded structure and by the fact that devitrification has advanced further. The author proposes to include all such banded rocks in a separate group of "eutaxitic glasses." Such rocks are widely distributed, occurring, as they do, in Hungary, Lipari, the Yellowstone Park, Teneriffe, Mexico, New Zealand, Ecuador, Japan, Shropshire, and Snowdon.

B. H. B.

Basaltic Hornblendes. By C. SCHNEIDER (*Zeit. Kryst. Min.*, **18**, 579—584).—The author gives the results of analyses of various basaltic hornblendes, and notes the connection existing between the percentage of ferrous oxide and the direction of extinction observed in the specimens examined. The hornblendes analysed were from the following localities : I. From the basalt-tuff of the Goldkaute, Vogelsberge (sp. gr. 3·249) ; II. From Bohemia ; III. From Härtlingen, in the Westerwald (sp. gr. 3·247) ; IV. From Hoheberg, near Giessen (sp. gr. 3·247) ; V. From Wolkenburg, in the Siebengebirge ;

VI. From the Laacher See (sp. gr. 3·245). The analytical results were as follows:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	Total.
I.	40·66	4·99	14·89	10·84	0·57	12·38	12·80	1·59	1·77	100·49
II.	39·75	5·40	15·00	7·86	2·89	14·16	12·97	1·92	1·61	101·56
III.	40·15	5·21	14·34	7·80	4·53	13·14	11·75	2·31	1·14	100·37
IV.	40·14	4·26	14·30	7·07	6·48	11·62	12·00	2·22	1·35	99·44
V.	39·29	4·86	16·57	9·18	3·19	10·40	12·90	?	?	—
VI.	39·05	4·68	15·45	6·39	7·34	11·28	13·75	1·34	0·94	100·22

For comparison, the author also gives four published analyses of hornblende (1) from a hornblende-andesite dyke in the Kaiserstuhl, (2) from the hornblende-diabase of Gräveneck, with 4·97 per cent. of titanium anhydride, (3) from Jan Mayen, and (4) from Bohemia, with 0·89 per cent. of titanium anhydride. The results of the author's analyses show that there is a great uniformity in the composition of the basaltic hornblendes, if the proportion of ferrous and ferric oxides is neglected. Many lavas, such as the leucite basalt of Ulrichstein and the basalt of Härtlingen, are very similar in composition. From the external characters of the basaltic hornblendes, the author was led to believe that they had been subjected to alteration. In order to obtain evidence on this point, he submitted specimens to the action of superheated steam at a red heat. Before ignition, the proportion of ferrous oxide and the angle of extinction of the various hornblendes were as follows:—

Laacher See	7·03 per cent.	8½°
Altenbuseck	6·27 „	6 to 8
Härtlingen	4·53 „	2 to 4
Wolkenburg	3·19 „	1 to 3
Bohemia	2·89 „	1
Ortenberg	0·57 „	0

After long ignition of all these varieties, the direction of extinction became straight, and all the ferrous oxide was converted into ferric oxide. The hornblendes became dichroic and acquired the characters of the varieties from Bohemia and Ortenberg. B. H. B.

Undetermined Silicates from the Kaiserstuhl. By A. Knop (*Zeit. Kryst. Min.*, **18**, 668).—A secondary mineral, probably identical with the "sideroklept" of Saussure, occurring in the limburgite of Sasbach, gave on analysis the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	MnO.	H_2O.	Total.
51·20	8·29	19·62	4·04	0·25	18·80	100·20

Protonontronite is the name given by the author to a dark-grey mineral which gave on analysis—

SiO_2.	Al_2O_3.	FeO.	MgO.	MnO.	CaO.	H_2O.	Total.
48·52	5·94	6·00	24·72	0·59	2·79	10·70	99·26

B. H. B.

Melanite from the Kaiserstuhl. By R. SOLTMANN (*Zeit. Kryst. Min.*, **18**, 628—629).—The author gives the results of an analysis of melanite from Oberrothweil, in the Kaiserstuhl:—

SiO_2.	TiO_2.	ZrO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	FeO.	CaO.
30·48	11·01	1·28	3·13	15·21	0·28	3·84	30·19

MgO.	$Na_2O + K_2O$.	Ignition.	Total.
2·28	1·65	0·19	99·54

The titanium may occur partly in the form of Ti_2O_3. The presence of zirconia is of interest, as it has not hitherto been detected in a mineral of the garnet group. B. H. B.

Composition of Idocrase. By A. KENNGOTT (*Jahrb. f. Min.*, 1891, i., Mem. 200—207).—The composition of idocrase (vesuvian), a mineral of which more than fifty analyses are known, has not yet been definitely formularised. The author has consequently recalculated the analyses available, and finds that the idocrases from the various localities consist essentially of the silicate

$$4(2RO,SiO_2) + 2R_2O_3,3SiO_2.$$

Besides this, however, and independent of it, there is a small proportion, as yet undetermined, which cannot be included in the silicate formula. This constituent is suggestive of the potassium fluoride in apophyllite, or of the calcium fluoride in apatite. It is, however, always an essential constituent of the idocrase. In idocrase, this portion is made up of water, possibly hydroxyl, potassium and sodium, and fluorine. As these substance occur in variable quantities, it has not been found possible to group them as a formula. (Compare Abstr., 1890, 221, 718.) B. H. B.

Composition of Slags. By J. H. L. VOGT (*Zeit. Kryst. Min.*, **18**, 669—678).—The author endeavours to determine the state of combination in which alumina is present in slags. He makes use of the following analyses:—

	SiO_2.	Al_2O_3.	CaO.	MgO.	MnO.	FeO.	K_2O.	Na_2O.	Total.
I.	55·60	5·86	24·90	11·07	1·09	1·30	—	—	99·82
II.	56·73	7·04	18·80	16·43	0·10	0·48	—	—	99·58
III.	54·00	5·37	27·75	8·67	0·91	2·06	0·51	0·53	99·80
IV.	54·68	4·79	24·70	13·87	0·97	1·85	—	—	99·86
V.	50·64	2·52	16·79	7·27	20·11	2·38	—	—	99·71

I. Coarsely crystalline blast-furnace slag from Sunnemo containing augite crystals; II. The same from Carlsdal; III. From Lófsjóen; IV. From Sunnemo; V. Blast furnace slag with augite and rhodonite from Hofors. On calculating these analyses, it is seen that aluminium is not, as in many natural augites, present as basic silicate, but as a so-called bisilicate. Analysis I, for example, gives the formula

$$R''SiO_3 + \tfrac{1}{11} Al_2Si_3O_9,$$

or expressed in detail,

$$CaMgSi_2O_6 + \tfrac{1}{20}\ CaMnSi_2O_6 + \tfrac{2}{10}\ Al_2Si_3O_9 + \tfrac{1}{4} - \tfrac{3}{10}\ Ca_2Si_2O_6.$$

In each case the ratio $Si : (R'' + \frac{1}{3}Al_2)$ is so nearly equal to 1 : 1 that the entire mass could solidify as augite. In slags containing less silica, examined by the author, augite does not separate out, but olivine or a silicate resembling melilite. In this way the proportion of silica in the residue is increased, so that it becomes possible for augite to separate out provided the mass does not rapidly solidify in the form of a glass. B. H. B.

Lithionite-granites. By F. v. SANDBERGER (*Zeit. Kryst. Min.*, **18**, 663—667).—In the lithionite-granites of the Fichtelgebirge, of the Erzgebirge, and of Northern Bohemia, there occurs an almost black mica, an analysis of which is given by the author. Analyses are also given of the orthoclase and other minerals met with in these rocks. The minerals met with in the cavities may be regarded as having been washed out of the surrounding rock. They differ from the tin ore veins chiefly in the predominance of tourmaline and albite, whilst tin ore and wolfram occur but sparsely. At Epprechstein the minerals have been deposited in the following order: 1. Mica (sp. gr. 2·825). 2. Albite. 3. Fluorspar. 4. Tourmaline, and 5. gilbertite, appear to have been formed simultaneously with the fluorspar. The gilbertite of Cornwall closely resembles this variety in its mode of occurrence. 6. Apatite. 7. Hyalite, in transparent crusts, frequently covers all the other minerals; 8. Lithophorite; 9. Lime uranium mica and copper uranium mica. The order in the case of the principal minerals is the same with the filling of the tin veins at Zinnwald, in the Erzgebirge. B. H. B.

Rocks of the Eruptive Mass of Jablonica. By C. v. JOHN (*Zeit. Kryst. Min.*, **18**, 661; from *Jahrb. k. k. Geol. Reichsanst.*, **38**, 343).—In the course of a geological investigation of the rocks of Jablonica, on the Narenta, the following analyses are given:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Ignition.	Total.
I.	46·80	33·50	0·90	15·85	0·56	0·21	2·23	0·67	100·72
II.	53·50	29·65	0·20	11·55	0·28	0·77	4·67	0·75	101·37
III.	57·50	25·45	1·40	9·15	0·55	0·89	4·65	0·45	100·04

I. Plagioclase from a gabbro in the midst of the mass; II. Plagioclase from an augite-diorite on the southern edge; III. Plagioclase from an augite diorite from Schemnitz. B. H. B.

The Lautenthal Brine-Spring. By G. LATTERMANN (*Jahrb. f. Min.*, 1891, i., Ref. 248—249; from *Jahrb. preuss. geol. Landesanst.*, 1889, 259—283).—In the "Güte des Herrn" mine, at Lautenthal, in the Harz, a brine-spring has been known for 30 years, and is interesting on account of its abnormal constitution. The salt has the following composition, in grams per litre:—

	$BaCl_2$.	$SrCl_2$.	$CaCl_2$.	$MgCl_2$.	NaCl.	KCl.
I.	0·314	0·854	10·509	3·219	67·555	0·359
II.	0·318	0·899	10·120	4·360	68·168	0·458
III.	0·219	0·859	10·490	3·275	64·076	0·387

I. From the main spring; II. From the same, taken a year later; III. From a point 70 metres from the shaft. Assuming that the flow amounts to 40 litres per minute, the amount deposited by the spring, deduced from Analysis I, would be as follows:—

	Per day.	Per year.
Barium chloride	18 kilos.	6,570 kilos.
Strontium chloride	49 "	17,885 "

It is highly probable that this spring is connected with the system of fissures of the Lautenthal ore-veins, and is derived from the rock-salt beds situated to the north of the Harz. B. H. B.

Organic Chemistry.

Tertiary Nitro-hydrocarbons of the Aliphatic Series. By J. Bevad (*Ber.*, **24**, 973—976).—Hitherto no tertiary nitro-compound of the aliphatic series has been prepared in a pure condition; Tscherniak obtained a liquid boiling at 90—100° from the product of the action of silver nitrite on tertiary butyl iodide, but gives no sufficient reason for regarding it as tertiary nitrobutane (this Journ., 1876, i, 902). In view of the close relations which would probably exist between such tertiary nitro-compounds and the aromatic nitro-compounds, the author has endeavoured to obtain the former by a reaction different from that employed by Tscherniak; and finds that tertiary nitrobutane is formed by acting with zinc methyl on bromonitropropane, $CMe_2Br{\cdot}NO_2$, and on dibromonitroethane, $CMeBr_2{\cdot}NO_2$, the first-named compound giving the better yield. To carry out the reaction, ethereal solutions of bromonitropropane are mixed and allowed to remain until the mixture no longer fumes on shaking, which takes several weeks. The mixture is then poured in small portions on to ice, and the precipitated zinc hydroxide dissolved in dilute sulphuric acid. The acid aqueous solution is extracted with ether, and the combined extracts evaporated and fractionated. By repeated distillation, a liquid is obtained boiling at 127—127·5°, and is further purified by cooling to −10° and separating the portions which remain liquid. Tertiary nitrobutane, $CMe_3{\cdot}NO_2$, is thus obtained as a crystalline mass which melts at 24°, boils at 126—126·5° under 748 mm. pressure, is miscible with alcohol, ether, and benzene, but insoluble in water, and has a specific gravity less than that of water. It has a caustic taste and peculiar acid odour, and gives off vapours which attack the eyes; it is insoluble in aqueous soda, and is not acted on by bromine or nitrous acid, and therefore corresponds in these respects with the aromatic nitro-compounds.

When reduced with tin and hydrochloric acid, it is converted into *tertiary butylamine*, the *hydrochloride* of which crystallises in characteristic plates, and melts at 270°.

If zinc ethide is substituted for zinc methide, the corresponding tertiary nitropentane and nitrohexane are obtained; nitroheptane is formed by the action of zinc ethide on chloropicrin, $CCl_3 \cdot NO_2$. These all resemble the nitrobutane in their properties, but the yield is very small. H. G. C.

The Supposed Isomeride of Acetylene Diiodide. By E. PATERNO and A. PERATONER (*Gazzetta*, **20**, 670—687).—In a previous paper (Abstr., 1890, 1219), the authors showed that whilst both the so-called diiodides of acetylene behave as though the two iodine atoms were symmetrically disposed, the percentage composition and molecular weight of the liquid iodide pointed to the formula $C_2H_2I_2 + C_2H_2$ as the most probable; this, however, does not satisfactorily explain the reactions of the liquid iodide described below, and the authors have therefore been led to reconsider their views.

When the solid iodide is treated with alcohol and zinc powder, it is decomposed, and an approximately theoretical quantity of acetylene is evolved; the liquid iodide, however, whilst giving up the whole of its iodine to the zinc, only evolves from 13 to 17 per cent. of the acetylene corresponding with the formula $C_2H_2I_2 + C_2H_2$. It was previously stated (*loc. cit.*) that the liquid iodide is converted into the solid compound by heating with water or by steam-distillation, and it is now found that the yield of solid iodide is generally about 20 per cent. The numerical results of the experiments seem to indicate that the liquid iodide only yields a quantity of acetylene theoretically corresponding with the amount of solid iodide it is capable of yielding. By passing acetylene first through glacial acetic acid and then into a mixture of iodic acid and alcohol, the authors have succeeded in obtaining a purer form of the liquid diiodide, which yields less solid iodide on heating with water (about 5 per cent.), and very little acetylene when treated with zinc.

The analyses of this product approximately agree with the formula C_2H_4IO, but the molecular weight determinations by Raoult's method point to a double molecule $C_4H_8I_2O_2$. It does not contain an OH group, as neither acetic nor benzoic chloride has any action on the pure product, nor has hydriodic acid until the temperature rises to 120°, when the mass is resinified. On distilling it with phosphorus pentachloride, acetic chloride, and iodine pass over; on reducing it with sodium amalgam, acetic acid is formed, together with traces of alcohol. Oxidation of the impure iodide with chromic acid also results in the formation of acetic acid. When heated with water in a reflux apparatus for several days, it is decomposed with the formation of acetic and oxalic acids. The acetyl group, which thus seems to be present in the liquid iodide of acetylene, contains neither of the iodine atoms, as on treatment with sodium and methyl iodide, the product consists of acetic acid, acetylene, ethane, an olefine, and traces of a heavy oil, but contains no derivative of either propionic or isobutyric acids.

Although the extreme solubility of the solid iodide in the liquid compound renders it impossible to isolate the latter in a state of purity, the authors hold the reactions of the latter compound can only be accounted for by regarding it as the acetate of a symmetrical di-iodovinyl, $CHI{:}CIAc$, and consider it as proved that the so-called isomeric diiodoethylenes have in reality completely different compositions. S. B. A. A.

Anhydrogeraniol, Olefinic Terpenes, and the Formation of Closed Carbon Chains. By F. W. SEMMLER (*Ber.*, **24**, 682—685).—The author has already shown (this vol., p. 540) that geranaldehyde, by loss of the elements of water, is converted into cymene, formation of a closed chain thus taking place. When geraniol is heated with potassium hydrogen sulphate, and the product distilled in a current of steam, a peculiar smelling oil is obtained, which after purification by repeated distillation over sodium boils at 172—176° (uncorr.), and has a sp. gr. of 0·8232 at 20° and $n_D = 1{\cdot}4835$ at 20°. From the analysis and determination of the vapour density, it was found to have the formula $C_{10}H_{16}$, and therefore belongs to the class of terpenes. In its physical properties, it differs, however, from the known members of that group, the sp. gr. being lower, and the molecular refraction much higher. It also yields a hydrocarbon $C_{10}H_{22}$, on reduction, and forms the compound $C_{10}H_{16}Br_6$ on treatment with bromine. The hydrocarbon must therefore contain an open chain of carbon atoms, and is the first representative of a new class of terpenes, for which the author proposes the name *olefinic terpenes*. Similar hydrocarbons have been obtained from coriandrol, linaloöl, and other olefinic camphors, and are being further investigated.

The results obtained in the author's various researches on this subject lead to the conclusion that the benzene derivatives occurring in plants are formed from compounds containing an open chain of carbon atoms. In order, however, that formation of a closed chain may take place, the parent substance must contain an aldehyde group, and a methylene group in the ϵ-position to it. Further, a methylene group must not occupy the α-position to the aldehyde group, as in that case also an unsaturated compound is formed.

If the benzene derivatives occurring in plants are really formed in this manner, no compound can occur in which the hydrogen atoms in the positions 1 : 2 : 6 are all displaced, or in which displacement has ever taken place in the position 6, the carbon atoms being numbered from the one in combination with an aliphatic radicle, usually allyl. All the benzene compounds hitherto examined by the author obey this rule. H. G. C.

Ammoniacal Derivatives of Mercuric Cyanide. By R. VARET (*Compt. rend.*, **112**, 535—536).—Gaseous ammonia, when passed into a solution of cupric bromide, forms a green precipitate, which redissolves and is followed by a blue, crystalline precipitate of cuprammonium bromide. The crystals and the mother liquor are added to an ammoniacal solution of mercuric cyanide, heated at 30°, and agitated until completely dissolved. The filtrate, on cooling, deposits hard, brilliant, blue crystals, of the composition $2HgCy_2,CuBr_2,4NH_3$. This compound alters but slightly when exposed to air, is almost insoluble in ammonia, and is decomposed by water. It can be heated at 100° for several hours without undergoing any appreciable change. The mutual action of cupric bromide and mercuric cyanide in presence of ammonia is quite different from their action in presence of water. Ammoniacal derivatives of the compound $HgCy_2,CuBr_2$ could not be obtained.

The compound $2HgCy_2,CdBr_2 + 3H_2O$ dissolved in aqueous ammonia at 40° yields small, white crystals of the compound $2HgCy_2,CdBr_2,4NH_3,2H_2O$, only slightly soluble in ammonia, and decomposed by water. At 100°, it becomes anhydrous without any loss of ammonia.

Cadmium iodide, when mixed with aqueous ammonia in quantity insufficient to dissolve it, and added in small quantities to an ammoniacal solution of mercuric cyanide, heated at about 40°, until it no longer dissolves, yields small, white crystals of the compound $HgCy_2,CdCy_2,HgI_2,4NH_3$. It is very unstable when exposed to air, and when treated with hydrochloric acid, is decomposed with precipitation of mercuric iodide and liberation of hydrogen cyanide. Heated in a small tube at a temperature insufficient to decompose mercuric cyanide, it evolves ammonia and yields a sublimate of mercuric iodide.

Ammoniacal compounds of mercuric cyanide and cadmium chloride seem to exist, but the author has not determined the conditions under which the compounds are formed in a pure state.

No evidence was obtained of the existence of ammoniacal compounds of mercuric cyanide with nickel chloride. C. H. B.

Action of Iodine on the Alcohols of the Fatty Series, $C_nH_{2n+2}O$. By J. TRAUBE and O. NEUBERG (*Ber.*, **24**, 520—521). When equal weights of ethyl alcohol and iodine are heated at 80° in a sealed tube for half an hour, an oily product is obtained which consists of ethyl ether and ethyl iodide, together with a small quantity of higher boiling products and unabsorbed iodine. Isobutyl alcohol and isoamyl alcohol, when heated at 100—110° with iodine, yield theoretical quantities of isobutyl iodide and isoamyl iodide respectively. A complete reaction takes place between iodine and ethyl ether at 200°. When small quantities of iodine are heated with ether above its critical temperature, the mixture of dark non-transparent gas gradually changes to a beautiful dark-red, then to bright-red, and finally becomes colourless. Bromine (1 vol.) acts readily on ethyl alcohol or ethyl ether (4—5 vols.) at 80°, and hydrogen bromide and ethyl bromide, together with higher brominated products, are formed. E. C. R.

Metallic Derivatives of Alcohols. By J. W. BRÜHL and H. BILTZ (*Ber.*, **24**, 649—650).—When borneol or menthol is dissolved in dry toluene or xylene and treated at the boiling point with sodium or potassium, a very violent action at first takes place, hydrogen is evolved, and a portion of the metal is dissolved. The action then becomes less violent, and continued heating is required for a considerable period of time before the alcohol takes up the theoretical quantity of the metal. It may be assumed from this that at first a molecular compound of the alcohol and the metallic derivative is formed, which is then gradually resolved into its components.

A similar reaction takes place with the simplest alcohols, and may be utilised for the preparation of alkyloxides free from alcohol. Methyl and ethyl alcohols dissolved in xylene, treated with sodium, behave just like borneol and menthol. A longer period of time is required, however, in these cases to complete the reaction, the sodium compounds being insoluble in the xylene, and forming a protecting layer on the surface of the sodium. Eventually, the whole of the alcohol is converted into alkyloxide, the latter remaining as a white, gelatinous mass suspended in the xylene. H. C.

Alkaline Derivatives of Erythritol. By DE FORCRAND (*Compt. rend.*, **112**, 484—487 and 532—535).—Cold concentrated solutions of erythritol and sodium hydroxide were mixed in the proportion of 1 mol. of the former to 1 to 2 mols. of the latter, and the solution was allowed to evaporate over phosphoric anhydride. The nature of the product is not affected by variations in the proportion of alkali between the limits stated. After some days, crystals separate which have the composition $C_4H_9NaO_4 + 2H_2O$. They alter rapidly in moist air, deliquesce like the alkaline alkyloxides, and are not dehydrated at 100°. In a current of hydrogen at 110—115°, however, the hydrate $2C_4H_9NaO_4 + H_2O$ is obtained, as a white, crystalline, deliquescent solid. After heating in hydrogen at 135° for about 12 hours, the total loss rises to 19·65 per cent., and the residue has the composition $C_4H_9NaO_4$.

Potassium hydroxide under similar conditions yields a crystalline hydrate, $2C_4H_9KO_4 + H_2O$, which must be heated at 140—150° for about 20 hours in a current of carefully dried hydrogen in order to expel all the water; the residue has the composition $C_4H_9KO_4$.

The heats of dissolution of these products are as follows:—

$C_4H_9NaO_4,2H_2O$	−6·57
$C_4H_9NaO_4,\frac{1}{2}H_2O$	−1·06
$C_4H_9KO_4,\frac{1}{2}H_2O$	−4·35
$C_4H_9NaO_4$	+0·53
$C_4H_9KO_4$	−1·23

The heat of neutralisation of erythritol by sodium hydroxide (equal equivalents) is +0·69 Cal., and by potassium hydroxide +0·708 Cal.

The calculated thermal disturbances corresponding with the formation of the various hydrates under various conditions are given. The heats of formation from carbon (diamond), gaseous hydrogen and oxygen, and solid metal are +257·67 Cal. in the case of the sodium compound and +264·22 Cal. in the case of the potassium salt.

The heat developed by the action of solid sodium oxide on solid erythritol (+24·13 Cal.) is far greater than would correspond with a mere molecular combination of erythritol with sodium oxide. Moreover, the heats of formation of the various hydrates are of the same order of magnitude as the corresponding values for hydrated salts, and the relation between the different hydrates is also similar in the two cases. It follows that the products have the formulæ already given, and are not molecular compounds of the type $2C_4H_{10}O_4,K_2O$.

The heats of formation of the alkaline alkyloxides increase with the hydricity of the alcohol from which they are formed, thus: sodium methoxide +95·22 Cal., mono-sodium glycolloxide +150·82, mono-sodium glyceroxide +209·41, mono-sodium erythritoxide +257·67 Cal. C. H. B.

Formation of Sorbose from the Juice of Mountain Ash Berries. By A. Freund (*Monatsh.*, **11**, 560—578; compare Abstr., 1889, 480).—Since Pelouze first obtained sorbose (sorbin) in 1852, several investigators have attempted to prepare the sugar, but with varying results. Byschl and Boussingault were not successful in obtaining it, the latter having found the hexhydric alcohol sorbitol in the juice of the ripe mountain-ash berries (*Sorbus aucuparia*). According to Delffs, sorbose does not exist as such in the fresh juice of the berries, but is formed from the malic acid contained in it by the action of the ethyl alcohol derived from fermentation of the glucose present. The author confirms the view that sorbose is only formed after fermentation of the juice; but finds that its origin is not to be traced to the interaction of malic acid and alcohol. The most favourable conditions for the formation of the sugar are obtained when the juice is diluted to a sp. gr. of 1·09—1·06, and allowed to remain in open vessels for 10—12 months. If, after this time, a small quantity of the fermented liquid on evaporation yields an insignificant quantity of sorbose, the exposure to air is continued.

The formation of sorbose is really due to an oxidation of some substance present in the juice. The author thought that this substance would probably prove to be sorbitol, but on attempting to isolate that compound from the fresh juice, he obtained only a non-crystalline jelly, which gave a crystalline acetyl derivative melting at 100·2°, and an amorphous dibenzoic acetal (compare Meunier, Abstr., 1889, 223 and 479) melting at 190—191°. Sorbitol, on the other hand, gives a liquid acetyl derivative and a dibenzoic acetal melting at 160°. The non-crystalline jelly can be obtained from sorbose by reduction with sodium amalgam, thus proving that the formation of sorbose in the juice of the mountain ash berries is really due to its oxidation. That the jelly is very closely related to sorbitol, however, is shown by its conversion into that substance either by boiling its solution with very dilute nitric acid or more simply, by placing a crystal of sorbitol in a concentrated aqueous solution, which determines the formation of much crystalline sorbitol, the production of which may perhaps be explained by the assumption that an absorption of the elements of water takes place. G. T. M.

Wood-sugar (Xylose) and Wood-gum (Xylan). By E. W. Allen and B. Tollens (*Annalen*, **260**, 289—306; compare Abstr., 1890, 472).—The quantity of wood-gum (xylan) which can be obtained from wheat-straw by extracting it three times with 4—5 per cent. soda as described in its preparation from beech-wood (Abstr., 1889, 847) is 16·2 per cent. of the straw employed; the gum obtained in this way contains 3·76 per cent. of water and 28·27 per cent. of ash, consisting principally of silica, but it seems to be free from lignin, starch, cellulose, and hexoses; on distillation with acids, it yields from 9·17 to 19·19 per cent. of furfuraldehyde. A solution obtained by dissolving the gum (0·9794 gram = 0·6993 gram free from ash) and sodium hydroxide (1 gram) in water (50 c.c.) has a rotatory power of $[\alpha]_D = -84·1°$; on hydrolysis with 5 per cent. sulphuric acid (8 parts) at 100°, it yields 7·4 per cent. of pure crystalline xylose.

The yield of wood-gum from cherry-wood is 12·4 per cent.; the product contains 7·03 per cent. of water and 6 per cent. of ash, and on hydrolysis it gives 19·4 per cent. of crystalline xylose.

Loofah, free from seeds, yields 5·73 per cent. of wood-gum, dried over sulphuric acid; this product contains 3·26 per cent. of ash.

The gum obtained by extracting beet-root with boiling 5 per cent. soda gives arabinose on hydrolysis with 5 per cent. sulphuric acid, and is probably identical with Scheibler's metapectic acid.

When the cherry-red liquid prepared by warming xylose or arabinose with a solution of phloroglucinol in hydrochloric acid (Abstr., 1889, 847) is examined with the spectroscope, a very distinct and characteristic absorption band, situated almost exactly between the D- and E-lines, is observed; this behaviour distinguishes xylose and arabinose from substances, such as wood, which give a red coloration with phloroglucinol and hydrochloric acid in the cold (lignin reaction), no absorption band being observed in such cases. The bluish or yellowish-green solution obtained by treating xylose or arabinose with orcinol and hydrochloric acid and then dissolving the precipitate in alcohol also shows a very characteristic absorption band, situated between the C- and D-lines, but close to and partially overlapping the latter.

F. S. K.

Conversion of Starch into Dextrin by the Butyric Ferment. By A. Villiers (*Compt. rend.*, **112**, 435—437).—Finely divided potato starch was suspended in water in the proportion of 50 grams per litre, and steam was blown into the mixture until the temperature rose to 100°. The original liquid and the condensed water almost completely filled the flasks, and whilst still at 100° the liquid was mixed with a few cubic centimetres of a cultivation of *Bacillus amylobacter* and the flasks plugged with sterilised cotton wool. The vessels were kept at 40°, and, as a rule, the starch was completely liquefied in 24 hours. Fermentation was allowed to continue until the liquid no longer gave a blue coloration with starch, the time required varying with the homogeneity of the starch paste. The bacillus forms very mobile rectilinear rods, but towards the end of the change they thicken at one end and become perfectly motionless. Beyond this point the products of fermentation undergo no change. A very small quantity of gas is evolved, and the liquid has a distinct odour of butyric acid, but the quantity of this substance present does not exceed 0·3 per cent. of the original starch.

The products of the change are almost exclusively dextrins, which can be obtained by precipitation with alcohol, and may be partially separated by fractional precipitation. When dried, they form white, friable, very hygroscopic solids which combine with water with development of heat. The rotatory power of different fractions varies from +156° to +207·5°. Iodine gives a red colour with the most optically active products, the intensity of the colour decreasing with the rotatory power. The reducing power, however, varies inversely with the optical activity.

Rotatory power	156°	175·4°	207·5°
Reducing power	28·9	11·3	5·0

These dextrins are converted into sugars with very great difficulty; with water at 100°, the change is scarcely perceptible even after 48 hours, and with dilute sulphuric acid at 100°, the complete change requires about a day.

The absence of glucose and maltose from the products of fermentation indicates that the ferment converts the starch directly into dextrin without the intervention of any diastase secreted by the organism. C. H. B.

Fermentation of Starch by the Butyric Ferment. By A. Villiers (*Compt. rend.*, **112**, 536—538).—The alcoholic liquid from which the dextrins have been precipitated (preceding abstract) after some weeks deposits long, radiating crystals in amount equal to about 0·3 per cent. of the original starch. The crystals contain water and about 4 per cent. of alcohol; when exposed to air, they lose alcohol, absorb water, and become opaque, without any noteworthy alteration in weight. When recrystallised from warm water, the compound $2C_6H_{10}O_5 + 3H_2O$ is obtained in small, brilliant crystals which do not alter on exposure to air. The dried substance rapidly absorbs water from the air, but as soon as the quantity of water present corresponds with the formula, no further change takes place. The crystals which separate from the alcoholic solution have the composition $6C_6H_{10}O_5,C_2H_6O,5H_2O$.

The new compound *cellulosin* has a very slight sweet taste; 100 c.c. of water at 15° dissolve 1·3 grams, and at 70°, 15 to 16 grams. It has a high rotatory power; for the anhydrous compound $[\alpha]_D = +159·42°$. It does not melt, but burns with intumescence when heated, is not fermentable, and does not reduce alkaline copper solution. Dilute acids convert it completely into glucose, but the boiling must be continued for about 24 hours. It has no action on phenylhydrazine. Cellulosin does not preexist in the starch, but is a true secondary product of the action of the butyric ferment.

After the starch has been completely fermented, there remains an insoluble, bulky, white, flocculent residue which agglutinates on drying. It has the composition of cellulose, and is very slowly converted into glucose when boiled with dilute inorganic acids. C. H. B.

Levosin, a New Carbohydrate from Cereals. By C. TANRET (*Compt. rend.*, **112**, 293—295). Ground rye is extracted with alcohol of 50°, and the solution is mixed with twice its volume of alcohol of 94°, which precipitates a quantity of gum. The alcohol is partially distilled off, and the residue mixed with baryta-water until the addition of more merely produces a precipitate which redissolves immediately. It is then filtered, and mixed with a large quantity of hot, concentrated baryta solution, until a permanent precipitate is obtained; this precipitate is washed with baryta-water, decomposed by carbonic anhydride, and the solution concentrated, when levosin separates. To remove the small quantity of barium which it contains, it is dissolved in the smallest possible quantity of alcohol of 60°, mixed with just sufficient dilute sulphuric acid, and after removal of the barium sulphate, is precipitated with excess of alcohol of 95°.

Levosin, dried at 110°, has the composition $nC_6H_{10}O_5$, and determinations of the molecular weight by Raoult's method show that the value of n is 4. When the anhydrous compound is exposed to air, it increases in weight by 11 per cent., and forms a hydrate $C_{24}H_{40}O_{20} + 4H_2O$.

Levosin is a white, almost tasteless compound, which dissolves in water in all proportions, and is very soluble in dilute alcohol, but is almost insoluble in alcohol of 95°. It softens at 145°, and melts at 160°; sp. gr. = 1·62; rotatory power $[\alpha]_D = -36°$, which is not affected by the age of the solution or by temperature. It does not reduce Fehling's solution, is not affected by diastase, and does not ferment with beer-yeast. In presence of very dilute acid, it becomes hydrated with the same rapidity as cane-sugar, and the change is complete if the levosin is heated with water alone in sealed tubes at 100° for 24 hours. The rotatory power of the product is $[\alpha]_D = -76°$, and it consists of a mixture of 75 per cent. of levulose and 25 per cent. of a dextrose with a very feeble dextro-rotatory power.

Levosin is not attacked by boiling alkaline solutions, but with some bases it forms definite compounds. The barium compound, $Ba_2C_{24}H_{36}O_{20}$, is obtained by adding a solution of the carbohydrate to baryta-water; it is insoluble in baryta-water, and when treated with pure water yields the compound $BaC_{24}H_{38}O_{20}$. The latter is obtained by adding baryta-water to a solution of levosin until a slight, permanent precipitate is formed. The calcium compound, $C_{24}H_{38}CaO_{20}$, is obtained in a similar manner, and is precipitated by the addition of dilute alcohol. Levosin gives no precipitate with normal or basic lead acetate in aqueous solution, but in presence of alcohol it gives with the basic acetate a precipitate of the compound $C_{24}H_{36}Pb_2O_{20}$. With ammoniacal lead acetate, the compound $C_{24}H_{34}Pb_3O_{20}$ is precipitated. With acetic anhydride and sodium acetate, levosin yields a triacetate, and with acetic anhydride and zinc chloride, a tetracetate. When dissolved in cold fuming nitric acid, and precipitated by sulphuric acid, it yields a somewhat explosive mixture of dinitrates and trinitrates. It gives no coloration with iodine, and is oxidised by nitric acid to oxalic acid without the intermediate formation of mucic acid.

Levosin exists in rye to the extent of 0·8 per cent. of the dried grain; in green wheat it is present in the same proportion, but in ripe wheat only to the extent of 0·2 per cent. In the case of barley the variations are greater, the proportion in the green grains in July being 2·0 per cent. of the dried matter, whilst in the ripe grains there was only 0·1 per cent. Oats, whether green or ripe, and ripe maize, contain no levosin. C. H. B.

Cotton Dyeing. By L. Vignon (*Compt. rend.*, **112**, 487—489).—Thermochemical measurements have shown (Abstr., 1890, 553 and 939) that when cotton is placed in solutions of dyes, &c., it exerts a much smaller chemical effect than animal fibres under the same conditions.

Cotton, when heated in sealed tubes at 100° to 200° with 4 parts of ammoniacal calcium chloride or 4 parts of aqueous ammonia of 22°, undergoes very little physical change, but combines with 1·05 to 2·86 per cent. of nitrogen, which cannot be removed by washing with dilute acids or with water. When this product is placed in dilute sulphuric acid, it produces a much greater thermal disturbance (0·90 Cal. for 100 grams) than natural cotton under the same conditions (0·37 Cal. for 100 grams). The increased basic power of the cotton is also shown by the fact that when placed in solutions of dyes with an acid function, it acquires a somewhat deep colour, whilst ordinary cotton is but slightly tinted. C. H. B.

Normal Butylamines. By A. Berg (*Compt. rend.*, **112**, 437—439).—Normal butyl chloride was heated in sealed tubes at 120° for about 10 hours with an equivalent quantity of aqueous ammonia mixed with sufficient alcohol for complete solution. The reaction is complete, and from the residue which remains after distilling off the alcohol, the hydrochloride of the secondary base can easily be crystallised. If the mother liquors from this salt are treated with dilute sodium hydroxide solution, an insoluble mixture of the secondary and tertiary bases separates, and the liquid on distillation yields an almost pure solution of the monamine. No quaternary base is formed, and the proportion of the primary, secondary, and tertiary bases are 4, 7, and 1 respectively.

When the dilute aqueous solution of the monamine is mixed with ethyl oxalate in proper proportion, normal dibutyloxamide separates as a bulky precipitate almost insoluble in boiling water, but crystallising in silky needles from hot alcohol. The mother liquor contains butylamine, butyl oxamate, and normal butylamine oxalate. Calcium butyloxamate crystallises from hot water in very slender needles. Ethyl oxalate behaves in a similar manner with amylamine and with isobutylamine, hence the formation of the three terms of dehydration seems to be general.

Dibutylamine hydrochloride is somewhat soluble in water, and crystallises in beautiful scales; the aurochloride crystallises in beautiful, slender, golden-yellow needles which are only slightly soluble in cold water, and melt under water below 100°, but when dry melt at 170° to a reddish oil. The stannochloride is very soluble, and separates from a boiling solution as a colourless oil which solidifies on cooling, but can be obtained in long needles by slow evaporation. The acid oxalate resembles the hydrochloride, and is not very soluble in water. It is, however, much more soluble than the corresponding salt of diisobutylamine. C. H. B.

Additive Products of Hexamethylenamine. By H. MOSCHATOS and B. TOLLENS (*Ber.*, **24**, 695—696).—With many metallic salts, solutions of hexamethylenamine give precipitates, which in some cases are additive products. The *compound*

$$4C_6H_{12}N_4,3HgNO_3\cdot OH,10H_2O$$

is formed with mercuric nitrate; auric chloride also gives a precipitate containing hexamethylenamine, whilst the precipitates produced by copper sulphate or lead nitrate are simply basic salts, and do not contain hexamethylenamine.

The crystalline dinitrate, described by Wohl, is precipitated from concentrated solutions of hexamethylenamine on the addition of concentrated nitric acid. Crystalline compounds are also obtained with aromatic hydroxy-derivatives. The subject is being further investigated by the authors. A. R. L.

The Simplest Normal Oxime, $CH_2{:}NOH$, and its Polymerides. By R. SCHOLL (*Ber.*, **24**, 573—581).—Formoxime is obtained when a solution of formaldehyde is treated with hydroxylamine. It cannot, however, be isolated, as, like formaldehyde, it exists only in solution and in the form of vapour, and on evaporation of the solution it polymerises and yields a solid, which the author considers to be trioximidomethylene.

Trioximidomethylene is best prepared as follows:—A cold saturated solution of hydroxylamine hydrochloride (20 grams) is mixed in a mortar with finely-powdered soda (41 grams) and filtered. The solution, which must be used at once, is slowly poured into a well-cooled 40 per cent. solution of formaldehyde (20 grams). The mixture soon becomes semi-solid, and to complete the action is allowed to remain all night, the product is then collected, washed with warm water (at 50°), alcohol (at 50°), and ether. It is a white, amorphous substance, insoluble in water and all ordinary organic solvents, but dissolves easily in dilute mineral acids and caustic alkalis; it is not precipitated from the latter on neutralisation. It does not melt, but at 132—134° is converted directly into vapour, and it commences to vaporise at 100°. The molecular weight of the solid cannot be determined. If hydrogen chloride is passed through the compound suspended in ether, a soluble hydrochloride is formed, and the percentage of chlorine indicates this to be a mixture.

Formoxime, $CH_2{:}NOH$, is slowly evolved in the gaseous state on heating the above compound at 100°, and quickly at 132—134°. A vapour density determination agreed with the formula $CH_2{:}NOH$. On cooling the gas, it condenses to trioximidomethylene.

Trioximidomethylene, when heated suddenly in a test-tube at the temperature of a Bunsen burner, decomposes with a more or less violent detonation into water and hydrocyanic acid.

When boiled for a short time with water, alcohol, or ether, it does not dissolve. On prolonged boiling with water or alcohol, or on heating with an indifferent solvent in a sealed tube at 100°, it forms a solution which is neutral, has a faint, characteristic odour, and is stable at the ordinary temperature if not stronger than 10—20 per cent. A molecular weight determination by Raoult's method gave 42·3; the theory for $CH_2:NOH$ is 45. By heating the solution with dilute sulphuric acid, formaldehyde and hydroxylamine are formed; by reduction with sodium amalgam, methylamine is produced. A characteristic property of formoxime in aqueous solution is its strong reducing power; silver nitrate is reduced at once, as also is mercuric oxide in presence of alkali. If mercuric chloride is added to the aqueous solution, a yellow mercury salt is precipitated which on warming yields mercurous chloride and then metallic mercury. Mercury nitrate also forms a yellow precipitate, which quickly changes to metallic mercury. Bromine-water is at once decolorised. With Fehling's solution in the cold, it gives an intense green coloration, changing to a blue-green, and on warming, cuprous oxide is deposited. Copper sulphate gives a brownish-green; ferric chloride gives an intense red, changing to brownish-red. E. C. R.

Oximes of Sugars. By H. Jacobi (*Ber.*, **24**, 696—699).—The fact that dextrose and galactose, like the simple aldehydes, yield oximes was first pointed out by E. Fischer, whilst the oxime of galactose was first obtained in the crystalline form by Rischbieth (Abstr., 1888, 40), and the corresponding derivative of mannose soon afterwards by E. Fischer and Hirschberger (Abstr., 1889, 687). In studying the oximes of dextrose and rhamnose, the author found that, when these were prepared from a mixture of hydroxylamine hydrochloride and sodium hydroxide, they could not, on account of their great solubility in water, be separated from the inorganic salts; this difficulty is, however, obviated by employing free hydroxylamine.

Dextrose oxime, $C_6H_{13}O_6N$, is prepared by exactly precipitating a not too dilute solution of hydroxylamine sulphate (20 grams) with a warm solution of barium hydroxide, and, after cooling, dissolving pure dextrose (20 grams) in the filtrate, the mixture being allowed to remain for three days. The solution is next decolorised by gently warming with animal charcoal, and is then evaporated to a syrup under diminished pressure at 40—50°. By allowing the latter to remain over concentrated sulphuric acid for 2—3 days, it solidifies to a crystalline mass, which is then freed from adhering mother liquor by spreading on a porous plate. The yield is 15 grams. It is purified by crystallisation from 80 per cent. methyl alcohol, and forms colourless, microscopic prisms, melts at 136—137°, and is very soluble in water, very sparingly in alcohol, and insoluble in ether. It has a faintly sweet taste, reduces Fehling's solution strongly on heating, and is lævo-rotatory, exhibiting bi-rotation. Its specific rotatory power in a 9 per cent. solution is $[\alpha]_{D20} = -2·2°$.

Rhamnose oxime, $C_6H_{13}O_5N$, is prepared in a similar manner to dextrose oxime, but crystallises more readily; the syrup which remains on evaporating its aqueous solution solidifies on triturating for a few minutes with a little methyl alcohol. The yield is 80 per cent. of the theoretical. It forms colourless tables, melts at 127—128°, and is very easily soluble in water, only sparingly in hot absolute alcohol, and insoluble in ether. It is dextro-rotatory, and exhibits bi-rotation; its specific rotatory power in a 9 per cent. solution is $[\alpha]_{D20} = 13{\cdot}6$.

The author has also determined the specific rotatory powers of the oximes of galactose and mannose, both of which, on account of their sparing solubility in cold water, could only be examined in 5 per cent. solutions. They are both dextro-rotatory and exhibit bi-rotation. The mean values of two determinations with each are as follows:—galactose oxime, $[\alpha]_{D20} = 14{\cdot}75$, and mannose oxime, $[\alpha]_{D20} = 3{\cdot}15$.

A. R. L.

Ethylsulphonacetone and Diethylsulphonacetone. By R. OTTO and J. TRÖGER (*Ber.*, **24**, 868—870).—*Ethylsulphonacetone*, $SO_2Et{\cdot}CH_2{\cdot}COMe$, is obtained by the action of sodium ethylsulphinate on chloracetone at the ordinary temperature; it is a yellow, viscid liquid, miscible with water, dilute alcohol, or benzene, but does not volatilise with steam. A crystalline compound is formed with hydrogen sodium sulphite. The *oxime* is deposited in colourless crystals melting at 101°. On treatment with potash, the sulphone is hydrolysed to acetic acid and ethyl methyl sulphone. Carbonic anhydride, acetic acid, and ethylsulphonic acid are formed on oxidation with potassium permanganate. The *bromo-derivative*, $SO_2Et{\cdot}CH_2{\cdot}CO{\cdot}CH_2Br$, is prepared by the action of bromine on an aqueous solution of the sulphone, and melts at 80°. *Diethylsulphonacetone*, $CO(CH_2{\cdot}SO_2Et)_2$, is obtained by the action of sodium ethylsulphinate on the preceding compound, and crystallises in small plates melting at 119°; it is readily soluble in water and dilute alcohol, but only sparingly in ether or benzene; the constitution of the compound is proved by the formation of ethyl methyl sulphone and ethylsulphonacetic acid on treatment with potash; the latter compound, on further hydrolysis, also yields ethyl methyl sulphone.

Phenylsulphonacetone has no physiological action. J. B. T.

Turkey Red Oil. By SCHEURER-KESTNER (*Compt. rend.*, **112**, 395—397).—The sulphonic acid in Turkey red oil can be separated from the free acid, or acid desulphonised during washing, by agitating the oil with a mixture of ether and water. The non-sulphonised acids dissolve in the ether, and the sulphonic acids dissolve in the water, from which they can be precipitated by a solution of sodium sulphate of 10° B. The proportion of sulphonic acid varies in oils prepared under seemingly identical conditions, and the solubility of the oil is determined by the proportion of the sulphonic acids. The degree of polymerisation is greater in the portion soluble in ether (mol. wt. = 472) than in the portion soluble in water (mol. wt. = 402).

The ricinoleosulphonic acid precipitated by sodium sulphate forms a hydrated, non-fluorescent syrup, which constitutes 40 to 50 per cent. of the most soluble Turkey red oil. Its composition agrees with that of diricinoleosulphonic acid, $COOH·C_{17}H_{32}·COO·C_{17}H_{32}·O·SO_3H$. After heating at 60°, it seems to contain 8 mols. H_2O.

The sulphonic and non-sulphonised acids in Turkey red oil can be estimated by making titrations with phenolphthaleïn and litmus respectively as indicators. Litmus becomes blue when all the sulphonic acid has been neutralised, but phenolphthaleïn does not change until all the non-sulphonised acid has also been neutralised.

Normal ricinoleïc acid, when treated with sulphuric acid, yields a product containing practically the same proportion of sulphonic and non-sulphonised acid as the product from resin oil.

C. H. B.

A New Optically Active Modification of Lactic Acid, obtained by Bacterial Decomposition of Cane Sugar. By F. SCHARDINGER (*Monatsh.*, **11**, 545—559).—According to Le Bel's hypothesis, optically inactive ethylidenelactic acid, OH·CHMe·COOH, since it contains an asymmetric carbon atom, should be separable into two active constituents, one dextrorotatory, the other lævorotatory. Until now only the former of these has been prepared (compare Lewkowitsch, Abstr., 1884, 296). The author has succeeded in obtaining the lævorotatory variety by fermenting cane sugar with a micro-organism which he has named *Bacillus acidi lævolactici.* The organism was obtained from a streamlet running through a Hungarian military station, the water having been examined owing to several cases of spleenic gangrene occurring amongst the horses. The bacillus forms short rods of about the same size as Heuppe's *Bacillus acidi lactici.* Under different conditions of growth, however, it assumes different forms; sometimes the individuals are joined in twos, sometimes they unite, producing long, thread-like masses. It appears to be without toxicological action on the smaller animals, is readily coloured by "carbolfuchsin," has a maximum activity at a temperature of 36°, is inert below 10° and above 40°, and is of anaërobic growth.

In order to study the products of fermentation, 30 grams of cane sugar was dissolved in 1 litre of water, to which 10 grams of ammonium chloride, 1 gram of disodium phosphate, 0·20 gram of magnesium sulphate, and 15—20 grams of calcium carbonate were added. The solution thus formed was sterilised and then inoculated with a pure culture obtained by Koch's method. In 1—1½ days, fermentation commenced, which attained its maximum in 4—5 days and ceased in 7—8 days. On distilling the product, a minute quantity of ethyl alcohol and much water passed over, and the residue (25 grams) consisted of a granular calcium salt, from which a zinc salt, $(C_3H_5O_3)_2Zn + 2H_2O$, crystallising in microscopic prisms, was obtained. In order to prepare the free acid, the zinc salt was dissolved in hot water, the metal precipitated with hydrogen sulphide, and the solution filtered and evaporated at a temperature of about 60°. The acid was further purified by treatment with ether, which left sulphur and some undecomposed zinc salt undissolved. On evaporating the ethereal solution, the acid was obtained in the form of a viscid, bright-yellow liquid, soluble in alcohol, ether, and water. The *silver salt*, $C_3H_5O_3Ag + \frac{1}{2}H_2O$, crystallises in long prisms, is very soluble in water, and rapidly turns yellow on exposure to light. The *calcium salt*, $(C_3H_5O_3)_2Ca + 4\frac{1}{2}H_2O$, is precipitated from its aqueous solution by absolute alcohol in the form of a felted mass of microscopic needles. The specific rotatory power of the acid is −4·3°; and, like paralactic acid, it has the property of forming an anhydride at ordinary temperatures, which anhydride has an opposite rotatory power to that of the acid from which it is obtained (compare Wislicenus, *Annalen*, **167**, 323, *et seq.*). The salts of the new acid are dextrorotatory, as those of dextrorotatory paralactic acid are lævorotatory.

When a mixture of equal parts of the zinc salts of dextrorotatory and lævorotatory ethylidenelactic acids was allowed to crystallise from a warm, saturated solution, the zinc salt of the ordinary fermentation lactic acid, $(C_3H_5O_3)_2Zn + 3H_2O$, was obtained, thus placing beyond doubt the complex nature of the last-named acid.

G. T. M.

Xylose. By E. Fischer and R. Stahel (*Ber.*, **24**, 528—538).—Xylose, as stated in a former communication (Abstr., 1890, 1399), combines easily with hydrogen cyanide to form a hexonic acid, whose lactone has the formula $C_6H_{10}O_6$. The latter is the optical antipode of d-gulonolactone (see p. 677); it is l-gulonolactone, and the sugar obtained from it l-gulose. By oxidation, l-gulonic acid is converted into l-saccharic acid.

l-Gulonic acid (xylosecarboxylic acid) is prepared by mixing xylose (100 grams) dissolved in twice its weight of water with the calculated quantity of hydrocyanic acid and a few drops of ammonia. The mixture turns bright brown in a few hours, and the action is complete in two days. The liquid is mixed with a solution of pure barium hydroxide (200 grams) in water (1200 grams), and boiled until all the ammonia is expelled. The baryta is precipitated quantitatively with sulphuric acid, the solution decolorised with animal charcoal, and evaporated to a syrup. Crystals of *gulonolactone* separate after a time. The mother liquors contain an acid which is probably an isomeride of gulonic acid. The yield of gulonolactone amounts to 60 per cent. of the xylose employed. It is purified by crystallisation from warm water or alcohol (60 per cent.), sinters at 179°, melts at 181° (corr. 185°), is easily soluble in hot water, but only sparingly so in cold water and absolute alcohol; it has a faintly sweet taste, and a neutral reaction; an aqueous solution, however, after a time becomes faintly acid. For a 9·15 per cent. aqueous solution, the specific rotation $[\alpha]_D = -55·3$ at 20°. The *basic barium* salt dissolves in a large quantity of hot water and crystallises in spherical aggregates of very slender needles. The *normal barium* salt is very soluble in water, and was not obtained crystalline. The *normal calcium* salt is obtained as a syrup, and crystallises after remaining a week or so. The *phenylhydrazide* is much more soluble in water than the corresponding compound of gluconic and mannonic acids, and cannot, in consequence, be used to precipitate gulonic acid. It melts at 147—149° (uncorr.), and decomposes at 195°.

l-Gulose is obtained by reducing a well-cooled solution (10 per cent.) of the lactone in the usual way with sodium amalgam. It is a colourless syrup, tastes sweet, is slightly dextrorotatory, and is not fermentable. The *phenylhydrazone* is obtained by adding a mixture of phenyl hydrazine (1 part) and acetic acid (50 per cent., 1 part) to a cold solution of the syrup (1 part) in water (2·5 parts). It crystallises from hot, absolute alcohol in slender, white needles, melts at 143° without decomposition, and is easily soluble in warm water, not so soluble in cold water and absolute alcohol. The *osazone* is obtained by heating the hydrazone or the sugar with excess of phenylhydrazine acetate for one hour on the water-bath; it crystallises from hot water in yellow, flocky masses, and turns reddish-brown on drying; when crystallised from dilute alcohol, it retains its yellow colour, melts at 156° without decomposition, and is remarkably soluble in hot water, differing in this respect from all known osazones of the natural hexoses. It resembles in this respect the osazones of xylose and arabinose, and has properties similar to those of β-acrosazone; it is probable that the latter is the inactive form of gulosazone.

i-Gulonolactone is obtained in well-formed crystals by crystallising a mixture of equal quantities of the l- and d-compound from water, and melts at 160°.

When l-gulonic acid is oxidised with nitric acid (sp. gr. = 1·2), l-saccharic acid is obtained, and is purified by means of its calcium salt.

The alcohol corresponding with dextrose and ordinary saccharic acid is sorbitol. Since l-gulose is a derivative of l-saccharic acid, it is to be expected that, on reduction, it would yield the unknown l-sorbitol; the product obtained is very like sorbitol, but does not crystallise so readily. It is obtained from alcohol as a colourless, gelatinous mass, which, when dried in a vacuum, forms a white powder, and melts at 70—75°. The benzal derivative is very like the derivative from ordinary sorbitol. Sorbitol in borax solution shows a faint dextrorotation; the new compound gives a lævorotation. The authors conclude that it is l-sorbitol.

From a consideration of the above results, the authors conclude that gluconic and gulonic acids have the same structure and similar configuration, and differ only in the position of the carboxyl group, as is shown in the (stereometric) formulæ (?)

$$COOH{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}OH \text{ and } OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}COOH.$$

Xylose, from the ease with which it is converted into furfuraldehyde, probably contains, like arabinose, a normal carbon chain; this is confirmed by the preceding results. Arabinose and xylose do not, however, bear the same relation to each other as gluconic and gulonic acids. For then they should both give the same alcohol on reduction. Arabinose, however, yields arabitol.

Xylose yields a new compound, *xylitol*, which forms a non-crystallisable syrup, and on treatment with benzaldehyde and sulphuric acid forms a crystalline benzal derivative. In borax solution it is optically inactive. Arabitol in borax solution is lævorotatory.

E. C. R.

Xylonic Acid. By E. W. ALLEN and B. TOLLENS (*Annalen*, **260**, 306—313).—*Xylonic acid*, an isomeride of arabonic acid, is formed when xylose (6 grams) is dissolved in water (30 grams), the solution treated with bromine (7 grams), and kept at the ordinary temperature until the halogen has dissolved; after removing the hydrobromic acid with lead and silver carbonate, and freeing the solution from metals with hydrogen sulphide, the filtrate is boiled with calcium carbonate, filtered, and evaporated, when the calcium salt remains as a syrup. The zinc and silver salts were prepared in like manner, but they could not be obtained in crystals. The *strontium* salt, $(C_5H_9O_6)_2Sr$, prepared by decomposing the calcium salt with oxalic acid and then treating the solution of the acid with strontium hydroxide, separates from dilute alcohol in efflorescent crystals containing about $8\frac{1}{2}$ mols. H_2O; the rotatory power of the salt, dried at 100°, is $[\alpha]_D = 12{\cdot}14°$, whilst that of the strontium salt of arabonic acid is $[\alpha]_D = 1{\cdot}96$. The rotatory power of a solution of xylonic acid, obtained by decomposing the strontium salt with the theoretical quantity of hydrochloric acid, was found to be $[\alpha]_D = 17{\cdot}48°$; the rotatory power of a solution of arabonic acid, prepared in like manner, is $[\alpha]_D = -45{\cdot}86°$. F. S. K.

Relative Properties of Dimethylglutaric and Trimethylsuccinic Acids; Stereo-isomeric Trimethylsuccinic Acids. By N. ZELINSKY and A. BESREDKA (*Ber.*, **24**, 459—478).—In their various attempts to synthesise trimethylsuccinic acid, Auwers and Jackson (Abstr., 1890, 1098), and Bischoff and Mintz (Abstr., 1890, 743; this vol., p. 290), have obtained substances which they believe to be the isomeric dimethylglutaric acid, identical with the symmetrical dimethylglutaric acid described by Zelinsky (Abstr., 1890, 132), as it has the same melting point of 102—104°, the same conductivity constant, and also yields a dibromo-compound, which would scarcely be expected were the product really a trimethylsuccinic acid.

The authors, however, believe that, notwithstanding this similarity, the compounds are not identical, for the "dibromodimethylglutaric acid" of Auwers and Jackson may be readily converted into the corresponding dihydroxy-compound, a stable substance which does not pass into a lactone, whereas Zelinsky's symmetrical dihydroxydimethylglutaric acid yields a monolactone with great ease. The explanation given by Auwers and Jackson of the formation of dimethylglutaric acid from ethyl α-bromisobutyrate and ethyl sodiomethylmalonate, is regarded by the authors as very probable, but they believe that this is only a subsidiary action, and that the chief portion of the product is in reality trimethylsuccinic acid, which in its physical properties closely resembles the lower melting dimethylglutaric acid. In favour of the glutaric constitution, Bischoff adduces the fact that the acid, when heated in a sealed tube, is converted into the higher melting dimethylglutaric acid; this fact, however, is really against that view, for Zelinsky's lower melting glutaric acid does not behave in the same manner, but, on the contrary, the higher melting acid is completely converted by hydrochloric acid at 200° into the lower melting acid; the symmetrical diethylglutaric acids behave in the same manner. Further, the lower melting dimethylglutaric acid forms an anhydride melting at 84—86°, which, on treatment with water, yields the higher melting acid.

Led by these considerations, the authors have attempted to synthesise trimethylsuccinic acid by a new method, namely, by acting on ethyl sodiocyanopropionate with ethyl α-bromisobutyrate, and hydrolysing the product with sulphuric acid. The following equations represent the reactions which take place :—

$$\mathrm{CN{\cdot}CMeNa{\cdot}COOEt + CBrMe_2{\cdot}COOEt = CN{\cdot}CMe(CMe_2{\cdot}COOEt){\cdot}COOEt + NaBr.}$$

$$\mathrm{CN{\cdot}CMe(CMe_2{\cdot}COOEt){\cdot}COOEt + 4H_2O = COOH{\cdot}CHMe{\cdot}CMe_2{\cdot}COOH + CO_2 + NH_3 + 2EtOH.}$$

The product of the hydrolysis is a mixture of acids all having the composition $C_7H_{12}O_4$. By repeated fractional precipitation with light petroleum from benzene solution, three acids were obtained; the first of these crystallises in rhombohedra and melts at 140—141° when quickly heated ; the second forms granules melting at 100—101°, and the third melts at 68—74°. The latter is probably a mixture, but requires further investigation; whilst the other two the authors regard as stereo-isomeric trimethylsuccinic acids, this substance containing an asymmetrical carbon atom. The second acid has almost the same melting point as symmetrical dimethylglutaric acid, but is more readily soluble in benzene; its conductivity constant *k* was found to be 0·0063, against 0·0055 for dimethylglutaric acid, whilst the constant for the acid melting at 140—141° was 0·0322. The conductivity of the two stereo-isomerides, as in the case of other stereo-isomeric succinic acids, is very different, whereas in the glutaric and adipic series this remains almost constant.

The isomeride melting at 100—101° is not identical with isopimelic or amylenepimelic acid (Abstr., 1878, 294), which melts at 100—106°. The supposed syrupy trimethylsuccinic acid recently described by Hell and Wildermann (this vol., p. 164) has not really the composition assigned to it, an error having been made in calculating the results of the analysis.

The authors have also observed that the conductivity of solutions of mixtures of stereo-isomerides remains constant in dilutions of 10—400 or more litres, but that on still further dilution, the constant decreases. To avoid errors, it is therefore necessary to examine the conductivity of extremely dilute solutions. H. G. C.

Acetonedicarboxylic Acid. By H. v. PECHMANN (*Annalen*, **261**, 151—162; compare Abstr., 1885, 138).—Acetonedicarboxylic acid, $CO(CH_2{\cdot}COOH)_2$, is best prepared in the following manner :—Finely divided, anhydrous citric acid (500 grams), obtained by heating the commercial acid at 145—150° for 1—2 hours, is placed in a flask of 4—6 litres capacity and a mixture of concentrated sulphuric acid (500 grams) and fuming sulphuric acid (500 grams), containing about 12 per cent. of anhydride, added; the flask is then fitted with a cork, through which passes a short piece of glass tubing. After 15 minutes time, the flask is placed on a water-bath, which has been previously heated to boiling, and the escaping gas is ignited, the heating being continued until the evolution of carbonic oxide ceases, which is usually the case in 30—45 minutes; the contents of the flask are then cooled to 0—5° and ice (600 grams) is gradually added, care being taken that no considerable rise of temperature occurs. On cooling again to 0—5°, the acetonedicarboxylic acid is deposited in crystals and is freed from the mother liquors by pressing it in flannel bags; the crude product, which is a grey or colourless powder, must be kept in an open vessel over sulphuric acid as, if placed in a closed vessel, it soon changes into a brown syrup and then decomposes into acetone and carbonic anhydride. The yield of crude acid, which contains about 5·0 per cent. of sulphuric acid and 36 per cent. of water, is 500—600 grams from 1 kilo. of commercial citric acid. The pure compound can be obtained by recrystallising the crude product from warm water, or ethyl acetate, or better, by shaking it with ether and evaporating the dried ethereal solution. It crystallises in colourless needles and melts at 135°, being decomposed into acetone and carbonic anhydride; the same decomposition takes place on boiling solutions of the acid. It is readily soluble in water and alcohol, but more sparingly in ethyl acetate, very sparingly in ether, and almost insoluble in chloroform, benzene, and light petroleum; in its aqueous solutions, ferric chloride produces an intense violet coloration and sodium nitrite a crystalline precipitate of dinitrosoacetone; on adding phenylhydrazine hydrochloride to a neutral solution of the acid in sodium carbonate, a colourless, crystalline precipitate is produced and carbonic anhydride is evolved. The salts of acetonedicarboxylic acid are rather unstable, and undergo decomposition into acetone and a carbonate even in the cold. The barium salt is precipitated in colourless crystals when a cold, concentrated solution of the acid is saturated with barium carbonate, and the filtrate mixed with alcohol; in aqueous solutions of the barium salt, most of the heavy metals produce a precipitate, silver nitrate and lead acetate giving a colourless, ferric chloride a brownish-red, and copper acetate a green precipitate which contains both barium and copper and is insoluble in hot water.

Ethyl acetonedicarboxylate, $C_9H_{14}O_5$, is prepared by passing a rapid stream of hydrogen chloride into a solution of the crude acid (200 grams) in absolute alcohol (200—250 grams), until the mixture becomes warm and begins to froth; the stream of gas is then moderated and the solution is saturated in the cold, otherwise decomposition sets in and carbonic anhydride is evolved. After keeping over night, the mixture is poured into ice-cold water containing a little sodium chloride, the solution repeatedly extracted with ether, the concentrated ethereal extract washed with small quantities of sodium carbonate until the washings give a turbidity on the addition of hydrochloric acid, then once with dilute sulphuric acid, and finally three times with water, dried over calcium chloride, and evaporated. The ethyl salt, prepared in this way, still contains alcohol and, as a rule, ethyl acetoacetate, but is otherwise tolerably pure; it can be obtained in a state of purity by dissolving it in sodium carbonate, or by converting it into the potassium or copper derivative (compare this vol., p. 673). Ethyl acetonedicarboxylate is a colourless oil of sp. gr. 1·1130 at 17°; it boils at 169—174° under a pressure of 50 mm. with only very slight decomposition, and under the ordinary atmospheric pressure its boiling point is about 250°; it is only sparingly soluble in water, but it dissolves freely in other neutral solvents and is also soluble in alkalis and alkaline carbonates; its dilute alcoholic solution gives a deep red coloration with ferric chloride and a dirty green precipitate with a solution of copper acetate. It dissolves sodium with evolution of hydrogen, and on adding anhydrous potassium carbonate to an ethereal solution of the oil, a colourless, crystalline potassium derivative is formed.

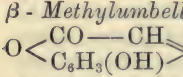
F. S. K.

Synthesis of Citric Acid from Acetonedicarboxylic Acid. By M. Dünschmann and H. v. Pechmann (*Annalen*, **261**, 162—166).—Citric acid can be obtained synthetically by treating ethyl acetonedicarboxylate with hydrogen cyanide in well-cooled ethereal solution and boiling the product, first with concentrated hydrochloric acid, and then with soda to ensure complete hydrolysis; the citric acid is isolated by means of its calcium salt, which is then decomposed with oxalic acid.

When ethyl acetonedicarboxylate is converted into the potassium derivative (compare next page), and the latter is boiled with water, ethyl acetoacetate separates from the solution as an oil.

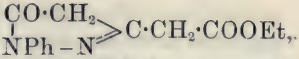
Acetonedicarboxylic acid readily undergoes decomposition into acetone and carbonic anhydride when it is heated alone or boiled with acids or dilute alkalis; when boiled with concentrated alcoholic potash, it yields malonic acid. F. S. K.

Condensation of Acetonedicarboxylic Acid with Phenols. By B. S. Burton and H. v. Pechmann (*Annalen*, **261**, 166—172).—*β-Methylumbelliferonecarboxylic acid* (*β-umbelliferoneacetic acid*),



$O<\begin{matrix}CO\text{—}CH\\C_6H_3(OH)\end{matrix}>C\cdot CH_2\cdot COOH$, is formed when an intimate mixture of resorcinol (25 grams) and crude acetonedicarboxylic acid (45 grams) (compare preceding page) is added to concentrated sulphuric acid (250 grams); the solution is kept over night, then poured into water, and the precipitated product purified by recrystallisation from alcohol or water. It crystallises in slender, lustrous needles, melts at 201—202° with decomposition, and is moderately easily soluble in boiling water and alcohol, but insoluble in cold water, ether, chloroform, and benzene; it separates from water in crystals containing 1 mol. H_2O, which is expelled at 110°, and its solutions in alkalis and alkaline carbonates show a blue fluorescence. The *silver* salt, $C_{11}H_7O_5Ag$, is a yellow compound, which turns black on boiling with water. The *ethyl* salt, prepared from ethyl acetonedicarboxylate and resorcinol, melts at 134°.

β-Methylumbelliferonecarboxylic acid is isomeric with the acid prepared by Michael from resorcinol, ethyl malonate, and sodium ethoxide (Abstr., 1888, 956); when heated above its melting point, it is converted into β-methylumbelliferone (m. p. 185—186°), a fact which shows that acetonedicarboxylic acid is an intermediate product in the formation of β-methylumbelliferone from citric acid, resorcinol, and sulphuric acid (compare Pechmann and Duisberg, Abstr., 1884, 66).

Ethyl methylphenylpyrazolonecarboxylate,  $\begin{matrix}\mathrm{CO\cdot CH_2}\\ |\\ \mathrm{NPh-N}\end{matrix}\!>\mathrm{C\cdot CH_2\cdot COOEt}$, is obtained when ethyl acetonedicarboxylate is heated with phenylhydrazine at 100°; it crystallises from dilute alcohol in lustrous prisms melting at 85°, and is insoluble in water, but soluble in ether, benzene, and chloroform; it combines both with bases and with acids, and gives the reactions of the pyrazolones. The free *acid*, $C_{11}H_{10}N_2O_3$, crystallises from boiling water in flat needles, melts at 134°, and is soluble in alcohol, but insoluble in ether, chloroform, and benzene; it combines with acids and with bases, and in its aqueous solution, ferric chloride produces a brownish-red coloration. On adding sodium nitrite to a sulphuric acid solution of the acid, a yellow, crystalline compound is precipitated, and when the acid is heated above its melting point it is decomposed into carbonic anhydride and methylphenylpyrazolone (m. p. 127°), identical with the compound obtained from ethyl acetoacetate.

When ethyl acetonedicarboxylate is boiled for a long time with an alcoholic solution of phenylhydrazine, yellow crystals are deposited; this substance is insoluble in acids, behaves in some respects like a hydrazone, and differs from the pyrazolone derivative described above.

F. S. K.

Alkyl Derivatives of Acetonedicarboxylic Acid. By M. DÜNSCHMANN and H. v. PECHMANN (*Annalen*, **261**, 173—190).—Ethyl acetonedicarboxylate yields metallic derivatives analogous to those of ethyl acetoacetate, but it contains four hydrogen atoms which are replaceable by alkyl radicles; of the two theoretically possible disubstitution products, only those of symmetrical structure can be obtained.

Ethyl potassioacetonedicarboxylate, $\mathrm{COOEt\cdot CHK\cdot CO\cdot CH_2\cdot COOEt}$, is obtained in crystals when ethyl acetonedicarboxylate is treated with the theoretical quantity of alcoholic potash, and the solution then mixed with a little ether; it crystallises from hot dilute alcohol in concentrically grouped needles, does not decompose at 100°, and is soluble in water, to which it imparts an alkaline reaction. The *dipotassium* derivative, $\mathrm{CO(CHK\cdot COOEt)_2}$, prepared in like manner, forms small, lustrous crystals and absorbs carbonic anhydride from the air; its aqueous solution has a strongly alkaline reaction, and, when boiled, gives off an odour of acetone. The *copper* derivative, $\mathrm{(C_9H_{13}O_5)_2Cu}$, separates from alcohol in green crystals, melts at 142—143°, and is insoluble in water, and only sparingly soluble in ether, but readily in hot benzene and cold chloroform.

Ethyl ethylacetonedicarboxylate, $\mathrm{COOEt\cdot CHEt\cdot CO\cdot CH_2\cdot COOEt}$, can be prepared by treating ethyl acetonedicarboxylate with sodium ethoxide and ethyl iodide in alcoholic solution. It boils at 207° under a pressure of 120—130 mm., and, in its alcoholic solution, ferric chloride produces a red coloration.

Ethyl αα'-diethylacetonedicarboxylate, $\mathrm{CO(CHEt\cdot COOEt)_2}$, prepared in like manner, boils at about 216° under a pressure of 130 mm.; its alcoholic solution is coloured violet by ferric chloride, but only after some time. The *triethyl* derivative, $COOEt\cdot CEt_2\cdot CO\cdot CHEt\cdot COOEt$, prepared from the preceding compound, boils at 223—224° under a pressure of 130 mm.; the *tetrethyl* derivative, $C_{17}H_{30}O_5$, boils at 231—232° under the same pressure.

When the ethyl salts of the homologues of ethyl acetonedicarboxylate are treated with excess of concentrated alcoholic potash at the ordinary temperature, the corresponding potassium salts are formed; a remarkable difference of behaviour is observed on decomposing these potassium salts with acids, for whereas the acids of symmetrical constitution can be easily prepared from the potassium salts and isolated in a crystalline condition, those of a symmetrical structure so readily undergo decomposition into carbonic anhydride and syrupy, ketone-like compounds that they cannot be obtained in a free state.

αα'-Diethylacetonedicarboxylic acid, $C_9H_{14}O_5$, crystallises from ether in colourless needles, melts at 112°, and is readily soluble in water, alcohol, and ether; when heated alone, or with water, it is decomposed with evolution of carbonic anhydride.

Tetrethylacetonedicarboxylic acid, $C_{13}H_{22}O_5$, crystallises from ether in small needles, melts at 70°, and is soluble in water and alcohol, but more sparingly in ether and benzene; it is decomposed either when heated alone or with water.

Ethyl methylacetonedicarboxylate is a liquid boiling at 195—200° under a pressure of 120—130 mm., and at 255° under the ordinary atmospheric pressure; its alcoholic solution gives a violet coloration with ferric chloride.

Ethyl αα'-dimethylacetonedicarboxylate, $C_{11}H_{18}O_5$, boils at 199—200° under a pressure of 130 mm., and at about 255—266° under the ordinary atmospheric pressure; it gives a violet coloration with ferric chloride, and when boiled with dilute sulphuric acid, it yields diethyl ketone.

Ethyl αα'-dibenzylacetonedicarboxylate, $C_{23}H_{26}O_5$, can be obtained by treating ethyl acetonedicarboxylate with benzyl chloride and sodium ethoxide; it separates from hot alcohol in crystals melting at 92°. The *mono-*, *tri-*, and *tetra-benzyl* derivatives are thick, yellow oils, and, as in the case of the corresponding ethyl derivatives, only the symmetrical compounds yield crystalline acids.

αα'-Dibenzylacetonedicarboxylic acid, $C_{19}H_{18}O_5$, prepared by hydrolysing the ethereal salt with alcoholic potash at the ordinary temperature, crystallises from a mixture of chloroform and ether in lustrous needles, and melts at 115—116°. The *silver* salt, $C_{19}H_{16}O_5Ag_2$, is colourless.

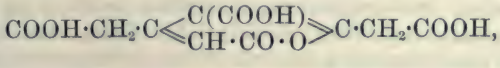
Tetrabenzylacetonedicarboxylic acid, $C_{33}H_{30}O_5$, crystallises from dilute alcohol in plates, and melts at 95°; the *silver* salt, $C_{33}H_{28}O_5Ag_2$, and most of the other metallic salts, are only sparingly soluble in water.

Dibenzylacetone, $CO(CH_2\cdot CH_2Ph)_2$, is obtained when the dibenzyl derivative of acetonedicarboxylic acid is boiled with acids or alkalis; this ketone is also produced by the dry distillation of calcium hydrocinnamate. It is a colourless oil boiling at 280—285° under a pressure of 130 mm. The *oxime*, $C_{17}H_{19}NO$, prepared by boiling the ketone with a dilute alcoholic solution of hydroxylamine hydrochloride, crystallises in colourless, lustrous needles, melts at 92°, and is insoluble in water, but readily soluble in alcohol, ether, and chloroform.

Ethyl diphenylpyronedicarboxylate, $\mathrm{CO}<\mathrm{\substack{C(COOEt):CPh \\ C(COOEt):CPh}}>\mathrm{O}$, is formed when ethyl sodacetonedicarboxylate is treated with benzoic chloride in ethereal solution; it crystallises from dilute alcohol in colourless plates, and is readily soluble in most ordinary solvents except water. It behaves towards alkalis like the corresponding dimethyl derivative (compare Conrad and Guthzeit, Abstr., 1888, 502), being decomposed into benzoic acid and acetophenone.

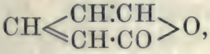
F. S. K.

Citracumalic Acid, a Condensation Product of Acetonedicarboxylic Acid. By A. Nieme and H. v. Pechmann (*Annalen*, **261**, 190—208).—*Citracumalic acid*,



$$\mathrm{COOH{\cdot}CH_2{\cdot}C}<\mathrm{\substack{C(COOH) \\ CH{\cdot}CO{\cdot}O}}>\mathrm{C{\cdot}CH_2{\cdot}COOH},$$

is formed by the condensation of acetonedicarboxylic acid, just as isodehydracetic acid is formed from acetoacetic acid, and cumalinic acid from formylacetic acid (compare Pechmann, Abstr., 1884, 1124). These three condensation products must all be regarded as 1 : 2 : 3-derivatives of a compound of the constitution

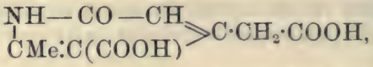


$$\mathrm{CH}<\mathrm{\substack{CH:CH \\ CH{\cdot}CO}}>\mathrm{O},$$

which the author names *cumalone;* it seems probable that all β-ketonic acids can be converted into carboxy-derivatives of cumalone by treatment with concentrated sulphuric acid.

Citracumalic acid is prepared by dissolving acetonedicarboxylic acid in concentrated sulphuric acid, and keeping the mixture for a long time at the ordinary temperature; the solution is then poured into ice-cold water, the precipitated acid separated by filtration, washed with a little water, and dried on porous plates. The crude product is a greenish-yellow powder, from which the pure acid is best obtained by recrystallising once from hot water, and then repeatedly extracting the dried crystals with boiling ether, when the pure compound remains as a colourless, crystalline powder. It begins to turn brown at 150°, and melts at 185° with decomposition, but it has no well-defined melting point; it is readily soluble in hot water and alcohol, but only sparingly in ether and glacial acetic acid, and is insoluble in chloroform and benzene. No metallic or alkyl salts were obtained in a pure condition. Citracumalic acid is very stable towards acids, but is decomposed when boiled with water or heated alone at 190—200°, yielding carbonic anhydride and isodehydracetic acid (m. p. 153°); when heated with soda-lime, it gives off an odour of mesityl oxide.

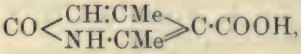
Lutidonecarboxylic acid (*pseudolutidostyrildicarboxylic acid*),



$$\left.\begin{array}{l}\mathrm{NH{-}CO{-}CH}\\ \mathrm{CMe{:}C(COOH)}\end{array}\right>\mathrm{C{\cdot}CH_2{\cdot}COOH},$$

is obtained in the form of its ammonium salt, when citracumalic acid is repeatedly evaporated with concentrated ammonia, and, on adding dilute sulphuric acid, the acid is precipitated as a dirty-grey powder. It crystallises from hot water in small, colourless needles, melts at 200—201° with evolution of carbonic anhydride, and is only very sparingly soluble in cold water, alcohol, and ether. The *silver* salt, $C_9H_7NO_5Ag_2$, is colourless. Lutidonedicarboxylic acid is partially decomposed by boiling water with evolution of carbonic anhydride, and, when heated above its melting point, it is completely converted into lutidone (m. p. 176°).

Lutidonecarboxylic acid (*pseudolutidostyrilcarboxylic acid*),



$$\mathrm{CO}<\begin{array}{l}\mathrm{CH{:}CMe}\\ \mathrm{NH{\cdot}CMe}\end{array}>\mathrm{C{\cdot}COOH},$$

is formed when the original condensation product of ethyl acetoacetate (compare Anschütz, Bendix, and Kerp, this vol., p. 172) is treated with concentrated ammonia at the ordinary temperature, the solution kept for 48 hours, and then evaporated. It separates from dilute acetic acid in crystals melting at 256—258° with evolution of carbonic anhydride, being converted into pseudolutidostyril; it is probably identical with the acid obtained by Collie from ethyl amidoacetoacetate (Abstr., 1885, 374). F. S. K.

Preparation of Pyromucic Acid. By H. SCHIFF (*Annalen*, **261**, 254—256).—The author again describes his improved method for the preparation of pyromucic acid from furfuraldehyde (*Annalen*, **239**, 374), as it has been tried by Bieler and Tollens with unsatisfactory results; when the operation is properly carried out, 28 grams of the pure acid and 25 grams of crude furfuralcohol are obtained from 56 grams of furfuraldehyde. F. S. K.

Solubility of Potassium Hydrogen Tartrate. By C. BLAREZ (*Compt. rend.*, **112**, 434—435).—The author has redetermined the solubility of potassium hydrogen tartrate in water, with results agreeing with those obtained by previous observers, although showing some differences at temperatures near 100°. The quantity of the salt, Q, contained in 100 parts of the solution at the temperature t, is given by the equation $Q_t = 0{\cdot}351 + 0{\cdot}00151t + 0{\cdot}00055t^2$, which for practical purposes may be replaced by the simpler formula $Q_t = 0{\cdot}369 + 0{\cdot}000569t^2$.

In presence of potassium chloride, the solubility of the potassium hydrogen tartrate is a function of the temperature and the quantity of chloride present, but is not continuous. With small quantities of potassium chloride, the quantity of tartrate precipitated is equivalent to that of the chloride added, but this ceases to hold good when the quantities of tartrate and chloride in solution are nearly equal.

When the quantity of chloride present is greater than the quantity of tartrate that the pure water could dissolve at the same temperature, the law of solubility is represented by a formula, which is a direct function of the temperature, but an inverse function of the square root of the potassium contained in the chloride added. $Q_t = (0{\cdot}0489 + 0{\cdot}000005216t^3)/\sqrt{K}$.

Potassium hydrogen tartrate is completely insoluble in a mixture of alcohol of 90° 100 parts, water 900 parts, normal potassium sulphate 4 parts, tartaric acid 2 parts, but dissolves if the hydrogen sulphate is substituted for all or part of the normal sulphate.

C. H. B.

Reduction of Saccharic Acid. By E. FISCHER and O. PILOTY (*Ber.*, **24**, 521—528).—The lactone of saccharic acid, as already stated (Abstr., 1890, 599), is easily reduced in acid solution by sodium amalgam. The aldehyde-acid which is formed the authors have now obtained in a crystalline condition, and shown it to be identical with glycuronic acid. By the further reduction of the acid they obtained a well-crystallised lactone, $C_6H_{10}O_6$, of a monobasic acid; this is identical with the product obtained by Thierfelder by the reduction of glycuronic acid. The authors, in agreement with Thierfelder, call the new acid gulonic acid, and the corresponding sugar gulose. On reduction of saccharic acid, evidently the carbonyl which is contained in gluconic acid is attacked, and the carbonyl of the new monobasic acid is at the other end of the carbon chain. The relation of these compounds is shown by the following formulæ:—

Glucose, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}COH$.
Gluconic acid, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}COOH$.
Saccharic acid, $COOH{\cdot}[CH{\cdot}OH]_4{\cdot}COOH$.
Glycuronic acid, $COOH{\cdot}[CH{\cdot}OH]_4{\cdot}COH$.
Gulonic acid, $COOH{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}OH$.
Gulose, $COH{\cdot}[CH{\cdot}OH]_4{\cdot}CH_2{\cdot}OH$.

Synthesis of glycuronic acid.—A solution of saccharic acid, obtained by decomposing the cadmium salt with hydrogen sulphide, is concentrated to a syrup, and heated for 5—6 hours on the water-bath to convert as much as possible into the lactone. 20 grams of this product is dissolved in 150 grams of water, well cooled, and mixed with 3 c.c. of sulphuric acid (20 per cent.), and 100 grams of sodium amalgam (2·5 per cent.). The mixture is constantly shaken, well cooled, and kept acid by constant additions of dilute sulphuric acid. When the first lot of amalgam is used up, a second lot of 100 grams is added, and then 50 grams. The solution is neutralised with soda, evaporated on the water-bath until a large quantity of sodium sulphate separates, 10 grams of concentrated sulphuric acid mixed with double the weight of water is added, and the mixture poured into eight times the quantity of hot absolute alcohol. The hot, filtered alcoholic solution is evaporated to one-tenth its bulk, diluted with water, neutralised with barium hydroxide, excess of baryta precipitated with carbonic anhydride, the baryta precipitated from the filtrate with sulphuric acid, and the liquid concentrated and neutralised while hot with white lead; the lead is precipitated with sulphuric acid, and the filtrate evaporated to a syrup. The lactone of glycuronic acid separates after a time, is filtered, dried on porous plates, and on recrystallisation from warm water is obtained in good, colourless crystals. It sinters when rapidly heated to 170°, and melts at 175—178°. For a 4 per cent. aqueous solution, the specific rotation $[\alpha]_D = +19{\cdot}1°$ at 20°. The yield of crystallised glycuronolactone amounts to only a few per cents. of the saccharic acid employed, but more is formed in reality, as is shown by the reducing power of the solution obtained by reduction of saccharic acid, and also by the greater yield of gulonolactone.

d.-Gulonic acid is prepared as follows :—20 grams of syrupy saccharic acid is mixed with 300 grams of sodium amalgam, and the liquid allowed to become faintly alkaline; after a time more amalgam is added, and the solution constantly neutralised with sulphuric acid. 400 grams of amalgam were added, with continuous shaking, in the course of four hours. When the hydrogen is no longer taken up, and the solution does not reduce Fehling's solution, all the glycuronic acid is converted to gulonic acid. The liquid is treated in a manner similar to that described above for glycuronic acid. Gulonolactone crystallises from warm water or 60 per cent. alcohol, and melts at 180—181°. For an aqueous solution of sp. gr. 1·0373, the specific rotation $[\alpha]_D = +55{\cdot}1$ at 20°. The yield of pure gulonolactone amounts to 10—12 per cent. of the syrupy saccharic acid employed, The *phenylhydrazide* is obtained by heating the lactone (1 part) with phenylhydrazine (1 part) and water (3 parts) for one hour on the water-bath; it melts at 147—149°, and is easily soluble in hot water and hot alcohol.

d.-Gulose is obtained from gulonolactone by reduction with sodium amalgam and sulphuric acid. It is a colourless syrup, and is easily soluble in water, but only very sparingly in absolute alcohol. With phenylhydrazine, it behaves like l.-gulose (see this vol., p. 667). When evaporated with nitric acid (sp. gr. = 1·15), it is converted into saccharic acid. A 10 per cent. aqueous solution at 30° showed no perceptible fermentation with yeast after remaining 24 hours.

The synthesis of d.-gulonic acid gives a general method for the production of new sugars, as the reduction of other bibasic acids of this group (mannosaccharic, mucic, and isosaccharic acids) will probably yield isomerides of the hexoses. E. C. R.

d.- and i.-Mannosaccharic Acids. By E. FISCHER (*Ber.*, **24**, 539—546).—By the oxidation of arabinosecarboxylic acid, Kiliani obtained a compound isomeric with saccharic acid, to which he gave the name metasaccharic acid (Abstr., 1887, 465). The optical isomerides of this acid are obtained from d.- and l.-mannonic acid. The author considers that arabinosecarboxylic acid in consequence of its relation to mannose would be better designated as l.-mannonic acid, and metasaccharic acid as mannosaccharic acid.

d.-Mannosaccharic acid is obtained by heating the lactone of d.-mannonic acid with one and a-half times the quantity of nitric acid (sp. gr. = 1·2) for 24 hours at 50°. The mixture is diluted with water, and evaporated to a syrup. The acid is then converted into the calcium salt, the latter decomposed with oxalic acid, and the filtrate evaporated to a syrup, which, on the addition of a little alcohol, crystallises. The product, which is the double lactone of d.-mannosaccharic acid, is purified by recrystallisation from hot alcohol. The yield amounts to 30—35° per cent. of the mannonolactone employed. It crystallises from hot alcohol or a small quantity of warm water in long, colourless needles of the formula $C_6H_6O_6$, sinters at 170°, melts at 180—190° with evolution of gas when heated quickly, reduces Fehling's solution rapidly when warmed, and is easily soluble in warm water, but somewhat sparingly in cold water. The aqueous solution is neutral when freshly prepared, but if left for 12 hours becomes strongly acid. For a 3·932 per cent. aqueous solution, the specific rotation $[\alpha]_D = +201{\cdot}8$ at 23°. The isomeric compound prepared by Kiliani gives an equal and opposite rotation. The compound is more easily prepared from mannose, as in this case the solution obtained by treating ivory-nuts with acid can be directly employed. The lactone dissolves easily in dilute alkali, and the solution turns yellow when boiled. The *calcium salt*, $C_6H_8O_8Ca$, is obtained as a crystalline powder by heating the lactone dissolved in water (100 parts) for half-an-hour with excess of calcium carbonate, decolorising the solution with animal charcoal, and evaporating in a vacuum. The *barium salt* is more soluble than the calcium salt, and crystallises in microscopic, elongated tablets. The *strontium salt* forms a crystalline powder. The *cadmium salt* is very insoluble in water, and is obtained in microscopic tablets on adding cadmium acetate to a solution prepared by adding acetic acid to the sodium salt.

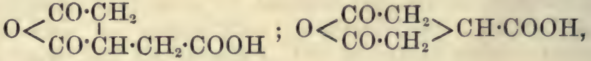
d.-Mannosaccharodiamide is obtained in colourless, rhombohedral crystals by shaking the dilactone with excess of ammonia. It darkens when quickly heated to 180°, melts about 189° with decomposition, and is decomposed with evolution of ammonia on boiling with alkalis.

The *monophenylhydrazide* is prepared by adding the finely-powdered dilactone (1 gram) to a cold solution of phenylhydrazine (1 gram) in acetic acid (50 per cent.). It crystallises from hot water in colourless needles, is easily soluble in hot water, but only sparingly in cold water or alcohol, dissolves in alkalis with precipitation of phenylhydrazine, turns yellow when heated rapidly to 185°, and melts at 190—191° with decomposition. The *dihydrazide*, $C_6H_8O_6(N_2H_2Ph)_2$, is obtained in pale-yellow plates by heating an aqueous solution of the lactone with excess of phenylhydrazine acetate. It turns yellow at about 200°, melts at about 212° with evolution of gas, and is quite insoluble even in hot water.

i.-Mannosaccharic acid is obtained by crystallising a mixture of equal parts of the d.- and l.-compounds, and also by the oxidation of i.-mannonolactone. It darkens about 170°, melts at 190° with decomposition, and is easily soluble in warm water, somewhat sparingly so in alcohol. Its aqueous solution is inactive, and when freshly prepared is neutral. The salts are very like those of the above d.-compound. The *diamide* crystallises in tablets, darkens at 170°, and melts at 183—185° with decomposition. The *hydrazide* is somewhat easily soluble in hot water, and melts at 190—195° with decomposition. The *dihydrazide* crystallises in colourless plates, melts at 220—225° with decomposition, and is quite insoluble in water.

Of the 10 bibasic acids with normal carbon chains indicated by theory, six are now known, namely, two active saccharic acids, two active mannosaccharic acids, mucic acid, and isosaccharic acid. The seventh acid which probably belongs to this group is obtained by heating galactonic acid with quinoline at 145°, and treating the product with nitric acid. It is optically active, and is distinguished from mucic acid by its greater solubility in water and alcohol. A similar acid is obtained by heating mucic acid with quinoline or pyridine at 140°, and is optically inactive. The author is engaged in working on these compounds. E. C. R.

Tricarballylic Acid. By W. O. Emery (*Ber.*, **24**, 596—602; compare Abstr., 1890, 133).—*Anhydrotricarballylic acid*, $C_6H_6O_5$, is prepared by heating tricarballylic acid with acetic chloride until solution takes place; after removal of the excess of acetic chloride, the residue crystallises from a mixture of chloroform and glacial acetic acid in slender needles; it melts at 132°, and is readily soluble in water or alcohol, but more sparingly in ether or chloroform. The same compound is also obtained by heating the acid in portions of 10 grams at 240—250° under reduced pressure; the anhydro-acid distils over at 233—235°; for this and similar operations, the author recommends a form of apparatus consisting of an ordinary Anschütz flask with the receiver ground to fit the narrow side tube of the distillation flask. The anhydro-acid is represented by one or other of the following formulæ,



$$\mathrm{O}<\begin{matrix}\mathrm{CO\cdot CH_2}\\ \mathrm{CO\cdot CH\cdot CH_2\cdot COOH}\end{matrix}\ ;\ \mathrm{O}<\begin{matrix}\mathrm{CO\cdot CH_2}\\ \mathrm{CO\cdot CH_2}\end{matrix}>\mathrm{CH\cdot COOH},$$

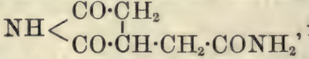
of which the first appears to be the more probable.

When the anhydro-acid is treated in ethereal solution with anhydrous ammonia, *hydrogen ammonium tricarballyamate*, $C_6H_{15}N_3O_5$, is formed as a white, hygroscopic powder; with silver nitrate, it yields the *normal silver salt* of tricarballyamic acid.

With phenylhydrazine, *tricarballylphenylhydrazidic acid* is obtained; its *calcium salt*, $C_{12}H_{12}N_2O_5Ca$, is crystalline.

Anilidotricarballylic acid is prepared by the action of aniline on the anhydro-acid at the ordinary temperature, and is a viscid liquid; the *silver salt*, $C_{12}H_{11}NO_5Ag_2$, is crystalline. At higher temperatures, tricarballylanilic acid is formed.

Orthotoluidotricarballylic acid, $C_{13}H_{15}NO_5$, prepared from the anhydro-acid and orthotoluidine at the ordinary temperature, crystallises in colourless, nodular aggregates, and melts at 143°. By the action of acetic chloride, *tricarballylorthotoluidic acid* is obtained, and is deposited from water in colourless crystals melting at 152°.



Tricarballylamidimide, $\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot CH_2}\\ \mathrm{CO\cdot CH\cdot CH_2\cdot CONH_2}\end{matrix}$, may be prepared by heating tricarballylamide at 220°, until ammonia ceases to be evolved.

1-2-3-*Tribenzoylpropane*, $CH_2Bz\cdot CHBz\cdot CH_2Bz$, is formed by heating tricarballylic chloride with benzene and aluminium chloride; it crystallises from alcohol in straw-coloured needles and melts at 137°. On warming with phenylhydrazine, a *monophenylhydrazone* is obtained; it is precipitated from glacial acetic acid, on the addition of water, in pale-yellow flocks, and melts at 57—60°. J. B. T.

Constitution of Leucine. By E. SCHULZE and A. LIKIERNIK (*Ber.*, **24**, 669—673).—α-Amidoisobutylacetic acid (amidocaproic acid), prepared from isovaleraldehyde, as described by Hüfner (*J. pr. Chem.* [2], **1**, 6), is identical with inactive leucine, which has been obtained from the active vegetable product by heating the latter with water and barium hydroxide at 160°. When the synthetical inactive amido-acid is fermented with *Penicillium glaucum*, a solution of an active acid is obtained; this active acid has the same rotatory power ($[\alpha]_D = -17·4°$) as the lævo-rotatory acid obtained by fermenting a solution of inactive leucine prepared from the natural amido-acid; the two compounds have, moreover, the same solubility in water, and they yield the same hydroxycaproic acid (m. p. 50—52°) on treatment with nitrous acid.

These results show that natural leucine is optically active α-amidoisobutylacetic acid. The leucine employed in the above experiments was obtained from a vegetable proteïd (conglutin); it is possible that leucine from other natural sources may have a different constitution. F. S. K.

Isopurpurates. By R. VARET (*Compt. rend.*, **112**, 339—341).—When zinc cyanide is added in small quantities to a boiling aqueous solution of picric acid, hydrogen cyanide is evolved and zinc picrate is formed, and the latter reacts with the excess of zinc cyanide. The liquid is heated for 36 hours with occasional addition of water, and the liquid gradually becomes redder and redder. It is then filtered and evaporated slowly on the water-bath, when crystals of zinc isopurpurate and ammonium isopurpurate separate. Sometimes the two salts combine, but this compound could not be obtained at will. The formation of ammonium isopurpurate is due to the substitution of ammonia during the action of the zinc oxide on the picric acid, and the quantity of the ammonium salt is greater the longer the period of ebullition. Zinc cyanide and ammonium picrate yield only ammonium isopurpurate, and no zinc isopurpurate.

Mercuric cyanide and picric acid yield no hydrogen cyanide and no isopurpurate, and this is true also with ammonium, potassium, barium, and strontium picrates, although in the last two cases compounds of mercuric cyanide and picric acid with barium or strontium picrate are precipitated.

Silver cyanide gives no isopurpurate when acted on with picric acid or potassium picrate. Copper cyanide yields no isopurpurate if heated with picric acid; it becomes bright-green, but the colour disappears on washing with water.

The displacement of hydrogen cyanide by picric acid from certain metals, and not from others, is in agreement with thermo-chemical data. C. H. B.

Alkyl Compounds of Cadmium and Magnesium. By P. LÖHR (*Annalen*, **261**, 48—87).—When finely-divided cadmium is heated with pure methyl iodide in exhausted sealed tubes at 100° for 40 to 50 hours, or at 110° for 20 to 25 hours, the methyl iodide is completely decomposed, a large quantity of gas is produced, and the metal is converted into a yellowish, crystalline mass, which consists principally of cadmium iodide, but contains small quantities, at the most about 12 per cent., of cadmium methyl iodide; analyses of the gaseous mixture showed that it consisted of ethane and small quantities of hydrogen or methane. On heating the yellowish, crystalline compound at about 110° in an atmosphere of carbonic anhydride, a mixture of cadmium dimethyl and methyl iodide collects on the cooler portions of the tube, but the quantity of this liquid is so small that the crystalline residues from 10 tubes only yield 90 to 100 drops. By careful fractional distillation in an atmosphere of carbonic anhydride, a considerable quantity (but not the whole) of the methyl iodide can be separated; analyses of the crude cadmium dimethyl, obtained in this way, showed that it contains about 76·37 per cent. of the pure organo-metallic compound, and about 23·97 per cent. of methyl iodide.

Cadmium dimethyl, $CdMe_2$, is a heavy, transparent, highly-refractive liquid, the vapours of which have an intensely repulsive odour, and a disagreeable metallic taste, producing nausea and vomiting. A mixture of cadmium dimethyl and methyl iodide, in the proportions given above, is not spontaneously inflammable at the ordinary temperature, but when gently warmed, it takes fire and burns with a luminous, smoky flame, giving off brownish-red fumes of cadmium oxide; it rapidly oxidises on exposure to the air, being converted into cadmium methoxide, $Cd(OMe)_2$, a solid, colourless compound, and it is quickly decomposed by water and dilute acids with development of heat and evolution of methane. It is completely decomposed by concentrated nitric acid, and, like the zinc alkyl derivatives, it destroys caoutchouc. It boils at 104—105° under a pressure of 738 mm., and solidifies to a mass of colourless crystals when cooled with ice and salt; zinc dimethyl solidifies almost immediately when cooled by the evaporation of liquid carbonic anhydride; zinc diethyl and mercury dimethyl also solidify under these conditions, but not so quickly, whereas mercury diethyl simply becomes viscous. Vapour-density determinations, made with crude cadmium dimethyl, gave results in agreement with those required by the molecular formula $CdMe_2$.

Attempts to prepare cadmium dimethyl by heating mercury or zinc dimethyl with cadmium or cadmium iodide were unsuccessful, the organo-metallic compound employed being simply decomposed into ethane and metal.

When finely-divided cadmium is heated with ethyl iodide, under the same conditions as those employed in the preparation of cadmium dimethyl, a reaction commences at 90°; the gas produced consists of about equal volumes of ethane and ethylene, but contains also small quantities of higher hydrocarbons, principally olefines, hydrogen, and probably also normal butane. The solid contents of the tube consist of a mixture of about equal parts of cadmium iodide and cadmium ethyl iodide and a little unchanged ethyl iodide; after exhausting and heating the tubes at 75—80° to expel the ethyl iodide, the residual colourless solid was heated in an atmosphere of carbonic anhydride; when the temperature had risen to 194—197°, a trace of a liquid showing all the properties of an organo-metallic compound distilled over, but practically the whole of the cadmium ethyl iodide was decomposed into cadmium, ethane, and unsaturated hydrocarbons. Other attempts to prepare cadmium diethyl were equally unsuccessful.

Finely-divided cadmium and propyl iodide react at about 70°, yielding a crystalline mixture of cadmium iodide and cadmium propyl iodide, and gaseous products; on heating the crystalline mixture at 185—187°, it is decomposed into cadmium, propane, and propylene, and only the least trace of cadmium dipropyl is formed.

In direct contradiction to the statement of Cahours (*Annalen*, **114**, 240), magnesium, either in the form of filings or ribbon, has no action whatever on methyl iodide at the ordinary temperature, and even at 200° the reaction is not complete; magnesium amalgam is also without action on the halogen iodide at the ordinary temperature. When, however, magnesium or magnesium amalgam is treated with methyl iodide in presence of ethyl acetate, an energetic reaction sets in, and a considerable development of heat occurs, but the mixture must be heated in sealed tubes at 110° for 40 to 50 hours before complete decomposition ensues. On opening the tubes, a gaseous mixture of ethane, ethyl acetate, and methyl iodide escapes, and there remains a dirty-grey, solid compound, which is probably either magnesium methyl iodide or a mixture of magnesium dimethyl and magnesium iodide; this grey substance is decomposed by water with great violence, yielding a very disagreeably-smelling, inflammable gas, and it retains this property even after it has been heated at 330° in an atmosphere of hydrogen.

When mercury dimethyl is heated in exhausted sealed tubes at 130° for 36 hours with a slight excess of the theoretical quantity of magnesium, in the form of filings, a dirty-yellow, solid compound is obtained, but no gaseous products are formed. Various analyses, and a careful examination of this yellow solid, showed that it is a mixture of metallic mercury and *magnesium dimethyl*. It takes fire spontaneously in an atmosphere of carbonic anhydride, burning with a brilliant display of sparks, and leaving a residue of magnesium, mercury, and carbon; it also takes fire when brought into contact with water, the gas evolved burning with a pale, slightly luminous flame; it is not decomposed when heated at 200° in an atmosphere of hydrogen, but at about 250°, a gas (in all probability ethane) is evolved. The above experiments show beyond doubt that magnesium dimethyl is a solid, non-volatile compound.

Magnesium, in the form of filings or ribbon, is without action on ethyl iodide at the ordinary temperature, but on prolonged heating at 100° in sealed tubes, the halogen iodide is decomposed, with liberation of ethane and other hydrocarbons, and a yellowish solid, consisting of a mixture of magnesium iodide and magnesium ethyl iodide, is formed; this solid product undergoes no change when heated at 280° in an indifferent atmosphere, and behaves, in other respects, like the mixture obtained from methyl iodide in like manner. In presence of a small quantity of ethyl acetate, a very violent reaction takes place between magnesium and ethyl iodide; after heating the mixture at 80° for several hours to complete the decomposition, the same products are obtained as when ethyl acetate is not added. On heating magnesium with mercury diethyl (or zinc diethyl) at 130°, small quantities of gaseous products and a voluminous, dirty-yellow substance are obtained; the solid product has the same properties as that formed from mercury dimethyl in like manner, and, doubtless, consists of a mixture of metallic mercury and solid magnesium diethyl.

Propyl iodide is decomposed by magnesium at a temperature of 75—80°. The principal gaseous product is propane, but considerable quantities of propylene and a little hydrogen are also formed. The solid product is a mixture of magnesium iodide and magnesium propyl iodide, which, in general behaviour, resembles the corresponding products obtained in like manner from the other halogen iodides.

F. S. K.

Purity of Benzene. By C. LIEBERMANN and A. SEYEWITZ (*Ber.*, **24**, 788—790).—The authors have observed that when commercially pure benzene (b. p. 80—82°) is mixed with phenylhydrazine, a compound is precipitated after a time in white plates of silvery lustre. On examination, it proved to be the compound

$$N_2H_4Ph\cdot CSS\cdot N_2H_2Ph,$$

and is formed by the action of carbon bisulphide on phenylhydrazine. The authors state that by means of this compound the carbon bisulphide is easily estimated. Crystallised benzene was found to contain no carbon bisulphide.

E. C. R.

Acetylation of Aromatic Halogen Substitution Products. By R. SCHWEITZER (*Ber.*, **24**, 550—552).—*Acetylbromobenzene*, C_6H_4BrAc, is obtained by gently warming a solution of bromobenzene in carbon bisulphide with acetic chloride in the presence of aluminium chloride. The viscous product is treated with water, extracted with carbon bisulphide, and the crystalline mass so obtained purified by boiling with animal charcoal in alcoholic solution. It crystallises in shining plates, melts at 51° (uncorr.), and has an agreeable odour resembling that of dried flowers; it is fairly easily soluble in alcohol, and very easily in ether, carbon bisulphide, light petroleum, acetic acid, and benzene.

Acetyliodobenzene, C_6H_4IAc, prepared in a similar way to the brominated derivative, crystallises from a mixture of light petroleum and ether in tablets, melts at 85° (uncorr.), has an agreeable odour, and is easily soluble in carbon bisulphide, alcohol, acetic acid, and benzene, less so in ether, and only sparingly in light petroleum.

Acetyl-α-bromonaphthalene is obtained by the action of acetic chloride on α-bromonaphthalene, in the presence of aluminium chloride in the cold. The product is treated with water and purified by fractional distillation. It is a pale-yellow oil, and boils at 345—347° (uncorr.) without decomposition.

Acetyl-β-bromonaphthalene.—The β-bromonaphthalene was obtained from β-naphthylamine by Sandmeier's reaction. The condensation with acetic chloride takes place in the cold; it is, however, better to heat the mixture. It crystallises well from petroleum, melts at 102° (uncorr.), and is very soluble in carbon bisulphide, acetic acid, and benzene, less so in alcohol and ether, and still more sparingly in light petroleum.

Paradiiodobenzene and 1 : 4-dibromonaphthalene gave no acetylation product when treated with acetic chloride and aluminium chloride in carbon bisulphide solution. E. C. R.

A New Reaction for Dinitro-compounds. By J. v. JANOVSKY (*Ber.*, **24**, 971—972).—The author has previously observed (*Ber.*, **19**, 2158) that the nitro-derivatives of azobenzene give a characteristic coloration with acetone and potash. This reaction is a general one for dinitro-compounds, but is not given by mononitro-compounds, and may, therefore, be used for determining the presence of the former. The reaction is carried out by dissolving a few milligrams of the compound in acetone, and adding aqueous potash drop by drop. A characteristic coloration is formed, the intensity of which is increased by the further addition of potash. Dinitrobenzene gives a reddish-violet coloration, which, after a time, becomes as dark as potassium permanganate, and is changed by acetic acid to dark-red, and by hydrochloric acid to yellow. 1 : 2 : 4-Dinitrotoluene gives a blue coloration, which is changed by acetic acid to violet-red; and α-dinitronaphthalene a bluish-red tint, which becomes eosin-red on addition of acetic acid. H. G. C.

Synthesis of Hydrocarbons. By R. HEISE (*Ber.*, **24**, 768—772).—Gustavson has shown that by the action of propyl bromide on benzene in the presence of aluminium chloride, isopropylbenzene is produced, and the author, after confirming this, has studied the reaction at a lower temperature.

Propylbenzene (b. p. 154—160°; 16 grams) is obtained, together with higher boiling products (4 grams) and unaltered benzene, when aluminium chloride (10 grams) is dropped into a mixture of propyl bromide and benzene (50 grams), cooled to −2°, and maintained at this temperature, with frequent shaking, for five hours. The propylbenzene was identified by means of its strontium and barium sulphonates, as well as by the melting point of its sulphonamide.

When propylbenzene (50 grams) is heated with aluminium chloride and dry hydrogen chloride for six hours at 100°, a mixture of meta- and para-dipropylbenzene (18 grams), benzene (6 grams), and unaltered or regenerated propylbenzene is obtained. To separate the dipropylbenzenes, the mixture is sulphonated by heating on the water-bath with fuming sulphuric acid (2 parts), and converted into the lead salts, from the aqueous solution of which, after concentration, needles and plates separate, the former in the smaller quantity. The needles, which prove to be the para-salt, are separated from the plates by treating the mixture with cold water, in which the former are sparingly soluble. *Metadipropylbenzenesulphonic acid* forms elongated tables, which easily deliquesce; the *lead salt* crystallises in very thin, glistening, rectangular, truncated tables, containing $1\frac{1}{2}$ mol. H_2O, easily soluble in cold water; the *barium salt* forms small, elongated plates, contains $1\frac{1}{2}$ mol. H_2O, and is readily soluble in water; whilst the *potassium salt* crystallises in well-formed tables, and is easily soluble in water. The *sulphonamide* separates from aqueous solutions in very long, delicate needles, and melts at 195°.

Parapropylisopropylbenzene is conveniently prepared from parabromocumene; the *sulphonic acid* crystallises in concentric tufts of needles, does not deliquesce in the air, and melts at 59—60°; the *lead* salt forms microscopic aggregates of needles, containing 1 mol. H_2O, and is somewhat sparingly soluble in water; the *calcium salt* crystallises in tufts of very long, flat, silky needles, belonging to the oblique system, which contain 8 mols. H_2O, and slowly effloresce in the air; whilst the *barium salt* forms delicate bunches of needles, somewhat sparingly soluble in water. The *sulphonamide* separates from water or dilute alcohol in long, delicate needles, and melts at 95—96°.

When propylbenzene is treated with isopropyl bromide and aluminium chloride at −2°, a mixture of para- and meta-propylisopropylbenzene is obtained, which is under investigation. A. R. L.

The Constitution of Cymene. By O. WIDMAN (*Ber.*, **24**, 439—456).—The researches of Fittig, Fittica, and others on cymene have led to the conclusion that this hydrocarbon is paramethylpropylbenzene, whilst the hydrocarbon cumene, with which it is closely related, is isopropylbenzene. This has been confirmed by Jacobsen (Abstr., 1879, 228), who again prepared a paramethylpropylbenzene synthetically and found it to be identical with the cymene obtained from camphor; he also prepared paramethylisopropylbenzene and found its properties to be quite distinct from those of cymene. There appeared, therefore, to be no doubt as to the existence of the normal propyl group in cymene, but from the ease with which the latter passes into compounds containing the isopropyl group, such as cumic acid, it was supposed that the propyl group in this compound readily undergoes an intramolecular change, passing into the isopropyl group. The author's experiments on thymol led him to the conclusion that this change depends on the nature of the group in the para-position, a methyl group causing a predisposition to the formation of propyl, and a carboxyl group to the formation of isopropyl (Abstr., 1886, 464). His further investigation has, however, shown that, whilst this conclusion holds when a methyl group is oxidised to carboxyl, no such conversion of propyl into isopropyl takes place when ethyl, acetyl, propyl, or isopropyl is converted into carboxyl. This result was so inexplicable from a theoretical point of view that the author undertook a thorough revision of the whole question of the constitution of the propyl group in cymene, and has obtained results in direct contradiction with those of most of the previous work.

The investigation consists in the preparation of paramethylpropylbenzene and paramethylisopropylbenzene, and a comparison of their derivatives with those of the cymene obtained from camphor. *Paramethylpropylbenzene* is readily obtained by the action of sodium on a mixture of parabromotoluene and propyl bromide. On distillation, by far the greater portion is obtained in the fraction 182—184°; and on redistillation, it boils for the most part at 183—184° (774 mm.), and has then a sp. gr. of 0·8682 at 15°. Under similar conditions, cymene boils at 175—177°, and has a sp. gr. of 0·8602 at 15°, and the odour of the two hydrocarbons is quite distinct. On sulphonation, the synthetical paramethylpropylbenzene yields a mixture of two sulphonic acids, which are separated by the different solubility of their barium salts. *Barium methylpropylbenzene-α-sulphonate* $(C_6H_3MePr^{\alpha}\cdot SO_3)_2Ba + H_2O$ is formed in much the larger quantity, and is sparingly soluble in cold water; it crystallises in lustrous, six-sided tablets, which are unaltered at 100°, and only lose their water of crystallisation slowly at 140—160°. Previous investigators have found this salt to contain 3 mols. H_2O. The *potassium* salt, $C_{10}H_{13}SO_3K + H_2O$, crystallises in large, four-sided tablets, which are dehydrated at 100°, whilst the *sodium* salt, which has the composition $4C_{10}H_{13}SO_3Na + 5H_2O$, loses 2 mols. H_2O in the exsiccator and the remainder at 100°. The *α-sulphonamide*, $C_{10}H_{13}SO_2NH_2$, forms large, transparent, monosymmetric tablets ($a : b = 1·684 : 1$; $\alpha = 45° \ 51'$), melts at 101—102°, and on oxidation yields the 1.2.4-sulphamidoparatoluic acid obtained by Hall and Remsen (Abstr., 1880, 257). The sulphonic group therefore occupies the position 2. *Barium methylpropylbenzene-β-sulphonate* can only be obtained pure by repeated fractional crystallisation, and then forms short, prismatic needles having the composition

$$(C_6H_3MePr^{\alpha}\cdot SO_3)_2Ba + 4H_2O;$$

it remains unaltered in the exsiccator, but becomes anhydrous at 100°. The *β-sodium* salt crystallises in needles, and the *β-sulphonamide* separates from benzene in lustrous scales melting at 112—113°.

Fittica states that both cymene and paramethylpropylbenzene yield the same substances by the action of nitric acid, namely, a solid and a liquid nitro-derivative. It has been shown, however, by v. Gerichten and Holleman (Abstr., 1878, 672; 1888, 454), that the solid compound has quite a different composition, and Widman and Bladin have proved that the liquid portion is not a nitro-compound, but consists chiefly of paratolyl methyl ketone (Abstr., 1886, 541). The author has, therefore, also examined the action of nitric acid on the synthetical methylpropylbenzene, and obtained a product which is not parotolyl methyl ketone, but is in all probability a nitro-derivative.

Paramethylisopropylbenzene is readily obtained from the parabromo-derivative of cumene (isopropylbenzene), by treating it with sodium and methyl iodide. The isopropylbenzene was prepared by acting on benzene with isopropyl bromide in presence of aluminium chloride, and converted by bromination into parabromisopropylbenzene boiling at 215—217° (corr.). The product obtained by the action of sodium and methyl iodide was too small in amount to purify completely by fractional distillation, but the portion boiling at 173—176° had exactly the same odour as cymene; on sulphonation, it yields an acid, the *barium* salt of which has the composition $(C_{10}H_{13}SO_3)_2Ba + 3H_2O$, and the characteristic appearance and properties of the salt obtained in the same manner from cymene. The *sulphonamide* crystallises from dilute alcohol or benzene in lustrous plates and melts at 115—116°, as does also that prepared from cymene.

From these results, there can be no doubt that cymene contains the isopropyl and not the normal propyl group, as hitherto supposed. The frequent change of one group into the other, assumed in these compounds, does not therefore take place, as all are in reality isopropyl compounds. The supposition that thymol and carvacrol are propyl derivatives only rests on their relationship to cymene, and therefore these, and in all probability all naturally occurring terpenes and camphors, are also isopropyl derivatives. H. G. C.

Cymene. By R. Meyer (*Ber.*, **24**, 970—971).—A reply to the communication of Widman (preceding abstract), in which the author points out that he did not, as might be assumed from Widman's paper, repeat and confirm Jacobsen's experiments, but simply analysed the barium salt of paraisopropyltoluenesulphonic acid, and found it in agreement with Jacobsen's result, to contain 1 mol. H_2O.

H. G. C.

Ethylpropylbenzene. By O. Widman (*Ber.*, **24**, 456—459).—This paper consists chiefly of a criticism of the results obtained by v. der Becke (this vol., p. 183), which the author regards as very incomplete. The two compounds described by v. der Becke as meta- and para-ethylpropylbenzenes yield amorphous potassium salts and liquid sulphonamides, and must therefore, in reality, be mixtures. The evidence adduced in proof of the formation of diethylbenzene and diisopropylbenzene is quite insufficient, and it is hardly probable, from analogy with other researches, that aluminium chloride should cause an elimination of side chains from substituted benzenes at the ordinary temperature, as is assumed by v. d. Becke. The latter was unable to obtain the two sulphonic acids of paraethylpropylbenzene described by the author (this vol., p. 45), but prepared a single sulphonamide melting at 84°. This is probably a mixture of the author's α- and β-sulphonamides, which melt at 112—113° and 108° respectively. The latter compound belongs to the hexagonal system, and forms rhombohedral, hemihedral crystals ($a : c = 1 : 1{\cdot}0365$). H. G. C.

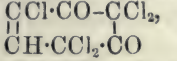
Preparation of Nitroso-compounds. By C. Willgerodt (*Ber.*, **24**, 592—595).—*Dinitrosonitrophenol*, $NO_2{\cdot}C_6H_2(NO)_2{\cdot}OH$, is formed when an alcoholic solution of picryl chloride is boiled with two molecular proportions of potassium iodide; formic acid or glacial acetic acid may be advantageously substituted for the alcohol. It crystallises from water in pale-yellow needles, which readily form feathery aggregates and melts at 122°. The compound is readily soluble in acids and organic menstrua, it does not change blue litmus paper, gives a red colour with concentrated alkalis, and may be sublimed without decomposition. Its tinctorial properties are greatly inferior to those of picric acid; it dyes wool yellow, is slightly bitter to the taste, does not give the nitroso-reaction, and is extremely stable towards oxidising agents.

Dinitrosonitrophenol-anthracene, $NO_2\cdot C_6H_2(NO)_2\cdot OH,C_{14}H_{10}$, is prepared by boiling anthracene with an alcoholic solution of dinitrosonitrophenol, and crystallises in long, yellowish-red needles melting at 160° (uncorr.). The corresponding *acenaphthene derivative*, $NO_2\cdot C_6H_2(NO)_2\cdot OH,C_{12}H_{10}$, is deposited in yellow needles melting at 168° (uncorr.). The *naphthalene compound*, $NO_2\cdot C_6H_2(NO)_2\cdot OH,C_{10}H_8$, crystallises in pale-yellow needles, and melts at 150—151° (uncorr.). *Dinitrosonitrophenolbenzene* is also crystalline, but decomposes on exposure to air.

Dinitrosonitrophenylazobenzene, $NO_2\cdot C_6H_2(NO)_2\cdot N_2Ph$ (m. p. 215—218°), may be prepared by the action of glacial acetic acid and potassium iodide or bromide on picrylphenylhydrazine, or by heating trinitrophenylazobenzene with glacial acetic acid and potassium iodide. Trinitroazobenzene, when reduced with iodine in glacial acetic acid solution, yields the second dinitrosoazo-derivative (m. p. 225°).

Dinitronitrosophenylparabromazobenzene may be obtained by the action of concentrated solution of hydrogen bromide in glacial acetic acid on picrylhydrazine or trinitrophenylazobenzene.

J. B. T.

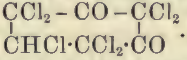
Action of Chlorine on Resorcinol. By T. ZINCKE and S. RABINOWITSCH (*Ber.*, **23**, 3766—3784; **24**, 912—923).—By the action of chlorine on resorcinol in chloroform or acetic acid solution, the first product is *trichlororesorcinol*, $C_6HCl_3(OH)_2$ ($Cl_3 = 2:4:6$), which crystallises in white needles and melts at 83°. On further chlorination, the pentachlororesorcinol, $C_6HCl_5O_2$, obtained by Stenhouse by acting on resorcinol with potassium chlorate and hydrochloric acid, is formed, and the author states that it is much more readily prepared by the new method. As was to be expected from Zincke's researches on the action of chlorine on other phenols (Abstr., 1888, 1277; 1889, 599, 967; 1890, 488, 1108), this is not a chloroxy-compound of the formula $C_6HCl_3(OCl)_2$, but has the constitution  $\begin{array}{l} CCl\cdot CO{-}CCl_2, \\ \| \qquad\qquad\quad | \\ CH\cdot CCl_2\cdot CO \end{array}$ the group, $C(OH){:}C\cdot Cl$, having been converted into $CO\cdot CCl_2$. It is not so unstable as stated by Liebermann and Dittler (this Journ., 1873, 62), the fact that the clear crystals became clouded being due to the absorption of water with formation of an unstable hydrate. It has all the properties described by Stenhouse, liberates iodine from potassium iodide solution, and yields trichlororesorcinol on reduction. The statement of Claasen (Abstr., 1878, 867) that pentachlororesorcinol on reduction yields a trichlororesorcinol melting at 69° is incorrect. Pentachlororesorcinol boils at 160° under 25 mm. pressure without decomposition, and is converted into hexachlorobenzene by phosphorus pentachloride at 200°.

When the pentachloro-compound is triturated with water, the hydrate is first formed, and then gradually dissolves; this solution, after a time, deposits a voluminous precipitate consisting of microscopic needles of a new acid; after crystallisation from light petroleum, it melts at 122—123°, and is readily soluble in alcohol, ether, and benzene, but scarcely at all in water. In place of water, a solution of sodium acetate may be employed and the solution precipitated with hydrochloric acid. The new compound is an acid of the composition $C_6H_3Cl_5O_3$, and does not yield trichlororesorcinol on reduction; it can, therefore, no longer contain a six-carbon ring, and does not contain a hydroxyl group, but on boiling with water loses carbonic anhydride forming a volatile oil, which, as will be shown later, is an orthodiketone, and has the constitution $CHCl_2{\cdot}CO{\cdot}CO{\cdot}CH{:}CHCl$. Hence it follows that the acid from which it is obtained must have the constitution $CHCl_2{\cdot}CO{\cdot}CCl_2{\cdot}CH{:}CCl{\cdot}COOH$, the formation of which from pentachlororesorcinol can be readily understood. It is, therefore, *dichloracetyltrichlorocrotonic acid.* The *amide* of this acid,

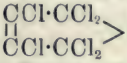
$$CHCl_2{\cdot}CO{\cdot}CCl_2CH{:}CCl{\cdot}CONH_2,$$

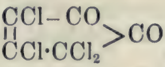
is obtained by the action of dry ammonia on a cold benzene solution of pentachlororesorcinol, and forms slender, colourless needles, melts at 166°, and is soluble in hot water and hot dilute hydrochloric acid.

If the decomposition of the acid with water be carried out in a distillation flask, the product of the reaction distils over with the steam, as an oil, which, after fractionating in a vacuum and recrystallisation from light petroleum, forms broad, yellow needles or plates, melts at 94°, and boils at 90—92° under 25 mm. pressure. It has an odour resembling that of quinone and chloropicrin and is readily soluble in alcohol, ether, benzene, and acetic acid. It has the composition $C_5H_3Cl_8O_2$, and is an orthodiketone, as it unites with orthotoluylenediamine forming a *quinoxaline* derivative, $C_{12}H_9Cl_4N_2$, which crystallises from light petroleum in yellowish, matted needles melting at 96°. With hydroxylamine, it yields a *monoxime*, $C_5H_3Cl_3{:}NOH$, crystallising from benzene in transparent, prismatic crystals melting at 110°. The only formula which such an orthodiketone, obtained from pentachlororesorcinol, could have is $CHCl{:}CH{\cdot}CO{\cdot}CO{\cdot}CHCl_2$, and it is therefore *dichloromethyl chlorovinyl orthodiketone.* By the action of alkalis, it is decomposed, monochloracetylene being formed, a reaction for which no thoroughly satisfactory explanation can as yet be proposed. It is also acted on by phosphorus pentachloride with formation of a substance which appears to be $CCl_2{:}CCl{\cdot}CCl_2{\cdot}CH{:}CHCl$, but has not been obtained pure.

When pentachlororesorcinol is subjected to further treatment with chlorine in chloroform or acetic acid solution, it takes up another two atoms of the halogen forming *heptachlororesorcinol* or *heptachlorometadiketohexamethylene*,  $\begin{array}{l}CCl_2-CO-CCl_2\\ \vert \qquad\qquad\quad \vert\\ CHCl{\cdot}CCl_2{\cdot}CO\end{array}$. It is most readily obtained from the mother liquors of the pentachloro-compound, which already contain it in quantity, by the further action of chlorine, distilling off the chloroform, and fractionating the residual oil under 25—30 mm. pressure. It then boils at 170—175°, the fresh distillate forming a colourless oil which gradually solidifies to a hard, crystalline mass; it melts at 50° and is readily soluble in alcohol, ether, benzene, and chloroform. On reduction with stannous chloride, it also yields trichlororesorcinol, but could not be converted into a compound of the composition $C_6Cl_6O_2$.

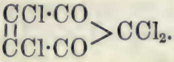
On treatment with water, oily products are obtained, but well characterised compounds containing an open chain of carbon atoms are formed by the simultaneous action of halogen and water.

Chlorine and water yield an acid of the composition $C_6H_2Cl_8O_3$, which crystallises from benzene in thick, lustrous, nodular aggregates of needles, melts at 139—140°, and is readily soluble in alcohol, ether, and hot benzene, sparingly in light petroleum. Its *methyl* salt, $C_7H_4Cl_8O_3$, obtained by the action of methyl alcohol and sulphuric acid, crystallises from dilute acetic acid in nacreous plates and melts at 68°. The acid readily undergoes decomposition, sets iodine free from potassium iodide, and on warming with water, loses carbonic anhydride and hydrogen chloride forming the compound $C_5Cl_4O_2$. The latter appears to contain a ring of five carbon atoms, for it behaves very like the compound  $\left.\begin{array}{l}\mathrm{CCl{\cdot}CCl_2}\\ \|\\ \mathrm{CCl{\cdot}CCl_2}\end{array}\right>\mathrm{CO}$, prepared by Zincke and Küster (Abstr., 1890, 754). For a substance of the composition $C_5Cl_4O_2$, containing a five-carbon ring, two formulæ are possible, namely:—



$$\left.\begin{array}{l}\mathrm{CCl{-}CO}\\ \|\\ \mathrm{CCl{\cdot}CCl_2}\end{array}\right>\mathrm{CO}$$

and



$$\left.\begin{array}{l}\mathrm{CCl{\cdot}CO}\\ \|\\ \mathrm{CCl{\cdot}CO}\end{array}\right>\mathrm{CCl_2}.$$

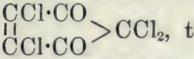
The compound does not react with orthodiamidotoluene, and on treatment with alkalis, yields a mixture of dichloracrylic acid, $CHCl\colon CCl\cdot COOH$, and dichloracetic acid, $CHCl_2\cdot COOH$, which proves that the second formula is correct.

For the acid $C_6H_2Cl_8O_3$, only two formulæ are possible, at whatever point the opening of the ring in heptachlororesorcinol takes place, namely:—

I. $CCl_3\cdot CO\cdot CCl_2\cdot CHCl\cdot CCl_2\cdot COOH$.
II. $CCl_3\cdot CHCl\cdot CCl_2\cdot CO\cdot CCl_2\cdot COOH$.

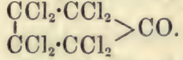
The formation of the above *tetrachlorodiketodihydropentene* does not decide between these two formulæ, but the authors regard the first as the more probable, according to which it is *trichloracetylpentachlorobutyric acid*. In favour of this view, is the fact that it is converted by alkalis into chloroform and a substance which behaves as a dicarboxylic acid.

The corresponding *dichlorobromopentachloracetylbutyric acid*, $CCl_2Br\cdot CO\cdot CCl_2\cdot CHCl\cdot CCl_2\cdot COOH$, is obtained by treating heptachlororesorcinol with bromine and water, and crystallises from benzene in beautiful, lustrous prisms melting at 149°, and readily soluble in alcohol and ether, sparingly in light petroleum. It closely resembles the chlorine derivative, and on boiling with water yields a mixture of the compounds $C_5Cl_4O_2$ and $C_5Cl_3BrO_2$, whilst with alkalis it yields dichlorobromomethane and the above-mentioned dicarboxylic acid.

Tetrachlorodiketodihydropentene,  $\left.\begin{array}{l}\mathrm{CCl{\cdot}CO}\\ \|\\ \mathrm{CCl{\cdot}CO}\end{array}\right>\mathrm{CCl_2}$, the preparation of which has already been described, crystallises from light petroleum in thick, transparent, rhombic tablets, melts at 75—76°, is volatile with steam, and has a peculiar, penetrating odour. It dissolves readily in alcohol, ether, benzene, and hot light petroleum, scarcely at all in water, and is, as previously stated, converted by alkalis into dichloracetic and α-β-dichloracrylic acids. The identity of the latter with the α-β-compound described by Bennett and Hill (Abstr., 1879, 616), and by Ciamician (*Ber.*, **16**, 2392), was proved by direct comparison, but the authors find the melting point to be 1° higher than previously given, namely, 87—88°, and have been unable to confirm Hill's statement that, on boiling with baryta-water, it yields carbonic anhydride, chloracetylene, and malonic acid.

Ammonia acts on the diketone in benzene solution forming a compound which crystallises in transparent prisms, melts at 190°, and probably consists of the *amide*, $CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CONH_2$. The corresponding *anilide*, $CHCl_2{\cdot}CO{\cdot}CCl{:}CCl{\cdot}CO{\cdot}NHPh$, is formed by the action of aniline in acetic acid solution, and forms slender, white needles melting at 162°. In alcoholic solution, aniline reacts in a different manner, forming a compound $C_{11}H_6Cl_3O_2N$, which crystallises in long, yellow needles, melts at 143°, and may possibly be a pyridone derivative.

By the action of phosphorus pentachloride on the ketone, a substance of the composition C_5Cl_8O is obtained, which might have the constitution



$$\begin{matrix} CCl_2{\cdot}CCl_2 \\ | \\ CCl_2{\cdot}CCl_2 \end{matrix}\!\!>CO.$$

Against this view is the fact that by the further action of phosphorus pentachloride at 300° it yields *perchlorethane*, C_2Cl_6, and an oily compound having the approximate composition C_3Cl_4O. The oxygen can therefore hardly be present as ketonic oxygen. H. G. C.

Nitration of Aromatic Amines. By E. NOELTING and L. STOECKLIN (*Ber.*, **24**, 564—572).—The nitration is effected by dissolving the amine in sulphuric acid and adding to the well-cooled solution a mixture of concentrated nitric and sulphuric acids. After remaining half an hour or so, the mixture is poured on to ice and neutralised with soda. It is advisable to add a small quantity of carbamide to the solution before nitration, in order to destroy any nitrous acid which may be formed. The following results were obtained :—

Metatoluidine gives as the chief product paranitrotoluidine [$NH_2 : Me : NO_2 = 1 : 3 : 4$], together with a small quantity of the two orthonitro-derivatives.

Orthoxylidine [$NH_2 : Me_2 = 1 : 2 : 3$] yields a mixture of the paranitro-compound [1 : 2 : 3 : 4] (m. p. = 114°) and the orthonitro-compound [1 : 2 : 3 : 6] (m.p. = 64—65°).

Orthoxylidine [$NH_2 : Me_2 = 1 : 3 : 4$] gives mainly the meta-compound [1 : 3 : 4 : 5] and a small quantity of the ortho-compound [1 : 3 : 4 : 2] or [1 : 3 : 4 : 6]. The former crystallises from alcohol in beautiful, reddish-yellow needles, and melts at 136—137°. The latter crystallises in brown needles, and melts about 80°.

Metaxylidine [$NH_2 : Me_2 = 1 : 2 : 6$] yields the *metanitro-compound* [1 : 2 : 6 : 3], which crystallises from alcohol in sulphur-coloured needles, and melts at 81—82°. The *acetyl* compound forms long, white needles, and melts at 170°. The same acetyl compound is obtained by nitrating acetometaxylidine dissolved in 5 parts of sulphuric acid with one molecular proportion of nitric acid (97—98 per cent.). If acetometaxylidine be nitrated in 10 parts of sulphuric acid with two molecular proportions of nitric acid, a *dinitro*-compound is obtained, which crystallises from alcohol in white needles, melts at 225—226°, and yields a *dinitroxylidine* melting at 177°. It has the constitution [$NHAc : Me_2 : (NO_2)_2 = 1 : 2 : 6 : 3 : 5$], since the diamine obtained from it by reduction does not combine with phenanthraquinone. When treated with nitrous acid, it readily yields diazo-compounds.

The author concludes from the above results that on nitrating the xylidines in sulphuric acid solution, the amido-group has no influence on the position taken up by the nitro-group, and that the latter displaces the same hydrogen atom as it does in the case of the xylenes.

Mesidine [$NH_2 : Me_3 = 1 : 2 : 4 : 6$], when treated under similar conditions to the above with one molecular proportion of nitric acid, yields mononitromesidine melting at 73—74° and identical with the product obtained by Maule, Knecht, and Ladenburg. With two molecular proportions of nitric acid, a dinitromesidine is obtained. It crystallises in beautiful needles, melts at 193°, and is identical with the product obtained by Fittig and Ladenburg.

Pseudocumidine [$NH_2 : Me_3 = 1 : 2 : 4 : 5$] does not easily yield a nitro-compound unless special precautions are taken, and resinous products are formed under most conditions. The best method of nitration is the following:—Finely powdered cumidine nitrate (10 grams) is gradually added to sulphuric acid cooled to −17° to −10°, the mixture poured on to ice and fractionally neutralised with alkali, when the ortho-compound separates first; the temperature must be kept below 0° and an excess of alkali is to be avoided. The product consists of 80—85 per cent. of the ortho- and 18—20 per cent. of the meta-compound. If 20 parts of sulphuric acid be used instead of 10 parts, the yield of meta-compound is increased to 25 per cent. The two nitrocumidines are also obtained by nitrating acetopseudocumidine in sulphuric acid solution.

Isodurene [$NH_2 : Me_4 = 1 : 2 : 3 : 4 : 6$] is also somewhat difficult to nitrate, and the same precautions must be taken as for pseudocumidine. *Nitroisodurene* crystallises from alcohol in yellowish-brown needles and melts at 87—88°. E. C. R.

Reactions of Oxyalkyl Derivatives of Dimethylaniline. By E. GRIMAUX (*Compt. rend.*, **112**, 290—293).—Metethoxydimethylaniline (dimethylmetaphenetidine), when treated with carbonyl chloride in presence of aluminium chloride, yields a blue colouring matter; whilst dimethylaniline itself, under the same conditions, yields a violet product. The blue substance has great tinctorial power, and gives a very pure blue shade on silk, wool, and cotton mordanted with tannin. When heated with sulphuric acid at 100°, it yields a red, fluorescent substance resembling the product obtained by heating dimethylmetamidophenol with dehydrating agents. From its mode of formation, it is probable that this colouring matter is a hexamethyl- and triethoxy-derivative of magenta,

$$CCl[C_6H_3(NMe_2)\cdot OEt]_3,$$

the introduction of the ethoxy-group having changed the colour from violet to blue.

Metethoxydimethylaniline yields a nitroso-compound, which resembles the corresponding derivative of dimethylaniline, but gives no compound similar to Meldola's blue with β-naphthol, and no derivative analogous to methylene-blue. With phthalic anhydride alone, the base undergoes no change, but in presence of zinc chloride or sulphuric acid, it forms a red, fluorescent compound which seems to be identical with rhodamine. When heated with arsenic acid at 175°, it yields a rose-coloured product which, seemingly, is not an oxidation product, but results from the formation and subsequent condensation of dimethylamidophenol. With phthalic chloride, a green colouring matter is formed similar to that obtained from dimethylaniline; with dimethylmetamidobenzoic chloride, a beautiful blue colouring matter is obtained; with chloroform and sodium hydroxide, a pink substance. When the base is gently heated with phenylsulphonic chloride, there is a violent reaction, and a blue compound is formed, which very rapidly changes to yellow. Benzaldehyde and zinc chloride, and "phenylchloroform" also produce colouring matters.

Dimethylorthoanisidine behaves in a very different manner. It yields no colouring matters with carbonyl chloride, phthalic anhydride, chloroform and sodium hydroxide, benzaldehyde, or "phenylchloroform." With sodium nitrite, it yields no nitroso-derivative analogous to nitrosodimethylaniline, and in this respect it resembles dimethylorthotoluidine. With arsenic acid at 175°, or with phenylsulphonic chloride, it yields a blue colouring matter, which, however, is formed when the hydrochloride is heated alone at 175—180°.

Neither the ortho- nor the meta-base yields colouring matters with cupric chloride.

The results show that the substitution of an oxyalkyl radicle for hydrogen greatly modifies the reaction aptitude, and also the tint of the colouring matters formed. The properties of the derivative are also largely dependent on the position of the substituted radicle.

C. H. B.

Action of Acid Chlorides on Orthodiamines. By A. Bistrzycki and G. Cybulski (*Ber.*, **24**, 631—634).—When orthotoluylenediamine (1 mol.) is heated with benzoic chloride (1 mol.) in benzene solution, the principal product is the dibenzoyl derivative (m. p. 263—264°); but a considerable quantity of the monobenzoyl derivative (m. p. 193—194°) is also formed; even when the conditions of the experiment are varied, the dibenzoyl derivative is always produced in the larger quantity, and no anhydro-base is obtained.

Diphenylacetyltoluylenediamine, $C_6H_3Me(NH{\cdot}CO{\cdot}CH_2Ph)_2$, is formed, together with the mono-derivative, when orthotoluylenediamine is heated with phenylacetic chloride in benzene solution. It crystallises from alcohol in long, lustrous needles, melts at 174—176°, and is moderately easily soluble in hot benzene, but almost insoluble in ether and light petroleum.

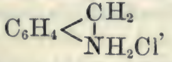
Phenylacetyltoluylenediamine, $NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CO{\cdot}CH_2Ph$, crystallises from hot alcohol in small, slender needles, melts at 194—195°, and is readily soluble in boiling benzene, but insoluble in light petroleum.

Orthotoluylenediamine and benzenesulphonic chloride react in benzene solution yielding the hydrochloride of the base

$$NH_2\cdot C_6H_3Me\cdot NH\cdot SO_2Ph,$$

and a very small quantity of a compound which is insoluble in dilute hydrochloric acid.

Acetic chloride converts orthotoluylenediamine into ethenyltoluyleneamidine when the reaction takes place at the ordinary temperature, but at 0° a considerable quantity of the diacetyl derivative of the diamine is also produced. F. S. K.

Paramidocarbinols. By O. FISCHER and G. FISCHER (*Ber.*, **24**, 723—729).—The simplest paramidocarbinol, paramidobenzyl alcohol, $NH_2\cdot C_6H_4\cdot CH_2\cdot OH$, has not hitherto been obtained. It is readily prepared by reducing the corresponding paranitrobenzyl acetate (*Annalen*, **147**, 343) with stannous chloride. The acetyl group is eliminated at the same time, and, after removal of the tin, a solution of paramidobenzyl alcohol hydrochloride remains. On addition of sodium carbonate solution, the base is deposited as a microcrystalline powder, and, on recrystallisation from alcohol, forms beautiful, colourless, silvery plates melting at 95°. It reduces silver from solutions of the nitrate. The *hydrochloride*, $NH_2\cdot C_6H_4\cdot CH_2\cdot OH,HCl$, crystallises in long, slender, colourless needles, and may be volatilised unchanged at 130° in a current of hydrogen. In air, however, it becomes yellow at 100—120°, and then colours silk yellow, but becomes colourless on redissolving in water. This change of colour is almost certainly due to elimination of water and formation of the compound  $C_6H_4<\begin{matrix}CH_2\\ |\\ NH_2Cl\end{matrix}$, which, from analogy with the rosanilines, should be coloured; the elimination of water is, however, never complete. The *hydrobromide*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot OH,HBr,$$

resembles the hydrochloride, and also becomes yellow at 100° in the air; the *oxalate*, $NH_2\cdot C_6H_4\cdot CH_2\cdot OH,2C_2H_2O_4$, crystallises in small, colourless needles, and melts with decomposition at 173°. The *acetyl* compound, $NHAc\cdot C_6H_4\cdot CH_2\cdot OH$, crystallises in slender, colourless needles, melts at 188°, and is almost insoluble in water and ether, but dissolves readily in acetic acid. The *benzoyl* compound, $NHBz\cdot C_6H_4\cdot CH_2\cdot OH$, is obtained by the action of benzoic chloride and aqueous soda, and crystallises from acetic acid in silvery plates melting at 223°. With benzaldehyde, amidobenzyl alcohol forms the *benzylidine* compound, $CHPh\colon N\cdot C_6H_4\cdot CH_2\cdot OH$, which crystallises in stellate aggregates of slender, greyish-white needles, and melts at 95°. The corresponding derivative obtained from salicylaldehyde forms yellowish-red, silky needles melting at 163°, and that from cinnamaldehyde crystallises in colourless plates, and melts at 155°.

The compound obtained by O. Fischer and Roser from benzhydrol and aniline, and further investigated by Fischer and Fränkel (Abstr., 1881, 587; 1888, 56), is identical with the paramidotriphenylmethane obtained by Baeyer and Löhr from paranitrobenzaldehyde and benzene, and is not, therefore, as previously supposed, an ortho-derivative. The triphenylmethanecarboxylic acid obtained from it must also be a para-derivative. H. G. C.

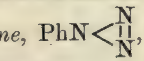
Sodium Compounds of Aromatic Anilides and Amines. By G. MINUNNI (*Gazzetta*, **20**, 721—723).—The author mentions that his attempts to prepare compounds of the type $COOEt \cdot CHAc \cdot NR'Ph$ by the action of the sodium anilido-compounds on ethyl chloracetoacetate were cut short by the publication of Paal and Otten's results (Abstr., 1890, 1415), and that he is at present examining the constitution of the alkaline anilido-compounds, reserving the right of further investigation in that field. S. B. A. A.

Action of Selenyl Chloride on Aromatic Tertiary Amines. By E. GODCHAUX (*Ber.*, **24**, 765—767).—*Selenodimethylaniline*, $Se(C_6H_4 \cdot NMe_2)_2$, is prepared by gradually adding 50 grams of selenyl chloride (1 mol.) dissolved in ether (30 c.c.) to a cooled solution of 10 grams of dimethylaniline (2 mols.) in ether (100 c.c.); a dark-brown mass separates which, after decanting the ether (see below), is dissolved in dilute hydrochloric acid, and an excess of sodium hydroxide added to the filtrate; the dimethylaniline is then removed by a current of steam, and the remaining oil washed successively with water, alcohol, and ether, when it solidifies; it is then pressed between filter-paper, dried, and crystallised from alcohol. The yield is small, and the compound is generally of a brown colour; it is obtained pure, however, by evaporating the above-mentioned ethereal solution, heating with water on the water-bath to remove the dimethylaniline, and crystallising from alcohol. It forms yellowish needles, melts at 124°, and is sparingly soluble in cold alcohol and ether. The sulphate, $C_{16}H_{20}N_2Se,H_2SO_4$, crystallises in long, colourless needles, melts at 55°, and is very easily soluble in water; the *picrate*,

$$C_{16}H_{20}N_2Se,2C_6H_3N_3O_7,$$

forms small, yellow plates, and melts at 135°.

Selenodiethylaniline, $Se(C_6H_4 \cdot NEt_2)_2$, is obtained in a manner similar to the dimethyl derivative, but the yield is greater. It forms colourless, asbestos-like needles, melts at 83°, and is moderately soluble in cold alcohol or ether, and very easily in the boiling liquids. The *hydrochloride*, $C_{20}H_{28}N_2Se,2HCl$, melts at 73°; the *picrate* crystallises from alcohol in small, yellow plates and needles, melts at 135°, and is easily soluble in hot alcohol. A. R. L.

Triazobenzene. By G. ODDO (*Gazzetta*, **20**, 798—802).—*Triazobenzene*,  $PhN<\begin{matrix}N\\ \|\\ N\end{matrix}$, may be prepared by the action of phenylhydrazine on diazobenzene tribromide. A mixture of diazobenzene chloride (0·1 mol.), bromine (20 grams), and concentrated hydrobromic acid (50 grams) is agitated in the cold, and phenylhydrazine (40 grams) added to the strongly-cooled product. The reaction takes place in accordance with the equation $PhN_2Br_3 + 2NHPh{\cdot}NH_2 = PhN_3 + C_6H_4{\cdot}NH_2,HBr + PhN_2H_3HBr$, and the yield is almost theoretical.

Triazobenzene is a pale-yellow liquid, having an odour of bitter almonds; it burns when lighted, with a slight explosion. It boils at 157·5—158° with partial decomposition. It may be distilled unchanged under reduced pressure. It is partially decomposed on exposure to the sun's rays. Its sp. gr. = 1·12399 at 0°/4°; its refractive index = 1·5597 for yellow light. It remains liquid at −33°.

S. B. A. A.

Constitution of the Amido-derivatives of Hydroxylamine. By G. Minunni (*Gazzetta*, **20**, 657—670).—The author has previously obtained (Abstr., 1890, 256) a white compound, $C_{13}H_{12}N_2O$, melting at 166°, by heating a mixture of benzhydroxamic acid with phenylhydrazine at 130—140°. This substance is not a hydrazone, as was then supposed, but is identical with Fischer's benzoylphenylhydrazine, $NHBz{\cdot}NHPh$ (Abstr., 1878, 308), and yields Tafel's methylbenzoylphenylhydrazine, $NHBz{\cdot}NMePh$, melting at 152—153° (Abstr., 1885, 1060) on treatment with methyl iodide. When benzhydroxamic acid and phenylhydrazine are heated together below 100°, only benzoylphenylhydrazine and gaseous products are formed.

If a mixture of benzhydroxamic acid and aniline in molecular proportion is heated, benzanilide is obtained. After discussing at length Lossen's and Tiemann and Krüger's (Abstr., 1885, 790) arguments in favour of the formulæ $OH{\cdot}CPh{\cdot}NOH$ and $NHBz{\cdot}OH$ respectively, as representing the constitution of benzhydroxamic acid, the author concludes that the second formula is strongly confirmed by the formation of benzoylphenylhydrazine and benzanilide from that compound, since the reactions occur under conditions unfavourable to molecular change, and as other amides yield analogous compounds under similar conditions.

S. B. A. A.

Amidoximes. By F. Tiemann (*Ber.*, **4**, 801—803).—The compounds obtained from aromatic amines and cyanogen have previously been represented by one of the three following formulæ:—

$$NH{:}C(NHR){\cdot}C(NHR){:}NH,\ NH{:}C(NHR){\cdot}C(NH_2){:}NR,$$
$$NR{\cdot}C(NH_2){\cdot}C(NH_2){:}NR;$$

the investigations of Vorländer (compare following abstract) show that these compounds exhibit a triple tautomerism. The paper concludes with some general remarks on the researches of A. Clemm (this vol., p. 699) and W. Krone (this vol., p. 700).

J. B. T.

Constitution of Disubstituted Oxalenediamidines. By D. Vorländer (*Ber.*, **24**, 803—825).—The term *oxalenediamidine*, instead of oxamidine, is applied to the compound

$$NH{:}C(NH_2){\cdot}C(NH_2){:}NH,$$

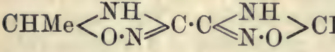
obtained from oxaldiimidodiethyl ether. Oxalenediparatolyldiamidine (cyanoparatoluidine) is already known, and is best obtained by heating recently prepared oxalimidoethyl ether with excess of paratoluidine at 100°; the product is dissolved in dilute sulphuric acid and precipitated with ammonia. Oxalenenedibenzyldiamidine (cyanobenzylamine) may also be obtained from oxalimidoethyl ether and benzylamine, by heating for 20 minutes at 100°, and then for 5 minutes at 110—120°. On heating oxalenediparatolyldiamidine at 150—160° in a current of hydrogen sulphide, ammonia and toluidine are eliminated, and a tarry residue is formed, from which no definite compound could be isolated. Oxalenediphenyldiamidine is decomposed by carbon bisulphide at 100°, hydrogen sulphide, phenylthiocarbimide, and resinous matters being produced; at lower temperatures, the amidine is scarcely attacked. Oxalenediparatolyldiamidine behaves in a similar manner.

Oxaleneparatolyldiamidodioxime, $NOH\dot{:}C(NHC_7H_7)\cdot C(NH_2)\dot{:}NOH$, is prepared by heating the tolyldiamidine with hydroxylamine hydrochloride or sulphate in alcoholic solution; it crystallises from water in small, white plates, melts at 175°, and is readily soluble in acids or alkalis; oxalenediamidoxime and paratoluidine are also formed during the reaction. Free hydroxylamine does not react with the amidine. The *dibenzoyl derivative*, $NOBz\dot{:}C(NHC_7H_7)\cdot C(NH_2)\dot{:}NOBz$, crystallises from alcohol in colourless needles, melts at 193—194°, and is readily soluble in alcohol or benzene.

Oxaleneparatolylamidineamidoxime, $NH\dot{:}C(NHC_7H_7)\cdot C(NH_2)\dot{:}NOH$, is obtained by treating the amidine with twice the theoretical quantity of hydroxylamine hydrochloride, sufficient soda being quickly added to liberate half the hydroxylamine; the product, after purification, crystallises from water in silvery, lustrous plates, melts at 147—148°, is insoluble in light petroleum, but readily dissolves in alcohol, chloroform, and benzene, and in alkalis and dilute acids. On further treatment with hydroxylamine, the compound yields toluidine and oxalenediamidoxime. The *hydrochloride*, $C_9H_{12}N_4O,HCl$, crystallises in flocculent needles. The *ethyl ether*, $NH\dot{:}C(NH\cdot C_7H_7)\cdot C(NH_2)\dot{:}NOEt$, is deposited from alcohol, on the addition of water, in lustrous plates melting at 132—133°. The *benzyl ether*,

$$NH\dot{:}C(NH\cdot C_7H_7)\cdot C(NH_2)\dot{:}NOC_7H_7,$$

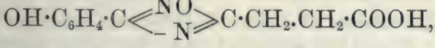
crystallises in needles and melts at 165°.

By the action of hydroxylamine hydrochloride on oxalenedibenzyldiamidine, oxalenediamidodioxime is formed. On warming this compound with acetic aldehyde, *oxalenedihydrazoximediethylidene*,  $\mathrm{CHMe}<\begin{matrix}\mathrm{NH}\\ \mathrm{O\cdot N}\end{matrix}>\mathrm{C\cdot C}<\begin{matrix}\mathrm{NH}\\ \mathrm{N\cdot O}\end{matrix}>\mathrm{CHMe}$, is obtained; it crystallises from benzene in colourless, slender needles, and melts at 198°. Diazoximediethenyl is produced on oxidation with potassium permanganate. *Chloraloxalenediamidoxime*, $C_8H_6N_4O_4Cl_3$, is prepared by gently heating the oxime with 7 parts of chloral, and crystallises from glacial acetic acid, on the addition of water, in lustrous plates melting at 196—197°. The compound is scarcely affected by concentrated sulphuric acid at the ordinary temperature; it does not react with alkaline copper solution or with ferric chloride; on treatment with alkalis, it yields ammonia and chloroform.

The formation of oxalenediamidines from oxalimido-ether appears to point to the first of the three possible formulæ (compare preceeding abstract); the reaction with carbon bisulphide is best represented by the second, whilst the analogy between oxalenediphenyldiamidine and aniline tells in favour of the third formula, as also does the action of hydroxylamine hydrochloride on di-substituted oxalenediamidines. The most probable explanation appears to be that these compounds afford the first observed example of triple tautomerism.

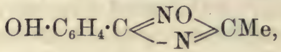
J. B. T.

Derivatives of Metahydroxybenzaldehyde. By A. CLEMM (*Ber.*, **24**, 826—833).—On treating metahydroxybenzaldehyde with phenylhydrazine in alcoholic solution, *metahydroxybenzenylphenylhydrazone*, $OH\cdot C_6H_4\cdot CH{:}N_2HPh$, is formed, and is deposited from benzene, on the addition of light petroleum, as a white, crystalline powder melting at 130°. The *oxime*, $HO\cdot C_6H_4\cdot CH{:}NOH$, prepared by the action of hydroxylamine at ordinary temperatures, is obtained from benzene in colourless, silky, lustrous crystals melting at 87·5°. *Acetylmetahydroxybenzonitrile*, $OAc\cdot C_6H_4\cdot CN$, is prepared by boiling the oxime with acetic anhydride for $2\frac{1}{2}$ hours; it crystallises from a mixture of benzene and light petroleum in long, transparent needles, melts at 60°, and is readily soluble in alcohol, ether, or hot water. On gently warming with dilute soda and acidifying, metahydroxybenzonitrile, $OH\cdot C_6H_4\cdot CN$, is formed. *Metahydroxybenzenylamidoxime*, $OH\cdot C_6H_4\cdot C(NH_2){:}NOH$, is prepared by heating the nitrile with hydroxylamine in alkaline solution at 60° for 6 to 8 hours, the solution is evaporated to dryness, extracted with alcohol, the alcohol removed, and the residue dissolved in water; it crystallises in aggregates of small, colourless needles, melts at 71°, and gives a dark-red coloration with ferric chloride. The *dibenzoyl derivative*, $OBz\cdot C_6H_4\cdot C(NH_2){:}NOBz$, is deposited from benzene, on the addition of light petroleum, in small, bright crystals and melts at 152·5°. On boiling the compound with water, metahydroxybenzenylazoximebenzenyl, $OH\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}CPh$, is produced; it has previously been prepared from metamidobenzenylazoximebenzyl and nitrous acid. The *benzoyl derivative*, $OBz\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}CPh$, crystallises from ether in microscopic needles and melts at 146°. *Metethoxybenzenylamidoxime ethyl ether*, $OEt\cdot C_6H_4\cdot C(NH_2){:}NOEt$, is obtained from the amidoxime by the action of ethyl iodide and sodium ethoxide, and crystallises from ether, on spontaneous evaporation, in colourless, well-developed needles melting at 109°. No monoethyl derivative could be isolated. On heating the amidoxime with succinic anhydride at 115°, water is eliminated and *metahydroxybenzenylazoximepropenyl-ω-carboxylic acid*,



$$OH\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}C\cdot CH_2.CH_2\cdot COOH,$$

is formed, crystallising from alcohol in colourless, transparent plates, and melting at 123°. The *silver salt* is crystalline. *Acetylmetahydroxybenzenylamidoxime*, $OH\cdot C_6H_4\cdot C(NH_2){:}NOAc$, is prepared by the action of acetic anhydride on the amidoxime at ordinary temperatures; it crystallises from ether in small plates and melts at 90°. On heating this compound above its melting point, or by boiling the amidoxime with acetic anhydride, *metahydrobenzenylazoximethenyl*,



$$\mathrm{OH\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}CMe},$$

is formed; this crystallises from alcohol, on the addition of water, in small plates, melts at 117°, and sublimes without decomposition.

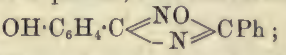
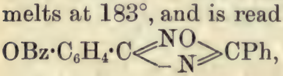
J. B. T.

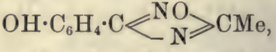
Parahydroxybenzenylamidoxime. By W. KRONE (*Ber.*, **24**, 134—841).—*Parahydroxybenzenylamidoxime*,

$$\mathrm{OH\cdot C_6H_4\cdot C(NH_2){:}NOH},$$

is prepared by treating parahydroxybenzonitrile with hydroxylamine under pressure at 70°; it melts at 153° with decomposition, and gives a dark-red coloration with ferric chloride. The *hydrochloride* is crystalline and melts at 179°. The *benzoyl derivative*,

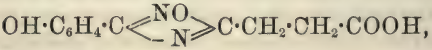
$$\mathrm{OH\cdot C_6H_4\cdot C(NH_2){:}NOBz},$$

is formed by the action of sodium ethoxide and benzoic chloride on the amidoxime; it crystallises from alcohol, on dilution with water, in colourless, slender needles, melts at 166°, and becomes red on exposure to air. The constitution of the compound is shown by the fact that when heated with potash, it is converted into *parahydroxybenzenylazoximebenzenyl*,  $\mathrm{OH\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}CPh}$; this crystallises from alcohol, on the addition of water, in colourless, lustrous plates, melts at 183°, and is readily soluble in alkalis. The *benzoyl derivative*,  $\mathrm{OBz\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}CPh}$, is prepared by the action of benzoic chloride and potash on the preceding compound; it crystallises from alcohol in needles and melts at 140°. *Dibenzoylparahydroxybenzenylamidoxime*, $\mathrm{OBz\cdot C_6H_4\cdot C(NH_2){:}NOBz}$, is formed by treating the amidoxime dissolved in potash, with excess of benzoic chloride, and crystallises from benzene in slender needles melting at 185°.

Acetylparahydroxybenzenylamidoxime, $\mathrm{OH\cdot C_6H_4\cdot C(NH_2){:}NOAc}$, obtained from the amidoxime and acetic anhydride at the ordinary temperature, crystallises from alcohol and melts at 122·5°. On heating the compound with water in a sealed tube at 100°, or by heating the amidoxime for a short time with a slight excess of acetic anhydride, *parahydroxybenzenylazoximethenyl*,  $\mathrm{OH\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}CMe}$, is formed; it crystallises from dilute alcohol in colourless, flat needles and melts at 185°.

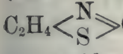
Parethoxybenzenylamidoxime ethyl ether, $\mathrm{OEt\cdot C_6H_4\cdot C(NH_2){:}NOEt}$, prepared by the action of ethyl iodide and sodium ethoxide on the amidoxime, is deposited from alcohol in long, dark-yellow, rhombic crystals melting at 84°. No monethyl derivative could be isolated.

Parahydroxybenzenylazoximepropenyl-ω-carboxylic acid,



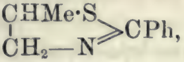
$$\mathrm{OH\cdot C_6H_4\cdot C{<}^{NO}_{-N}{>}C\cdot CH_2\cdot CH_2\cdot COOH},$$

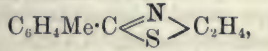
is formed on fusing the amidoxime with succinic anhydride at 115°; it melts at 176°, but is somewhat difficult to purify. The *silver salt* is colourless and crystalline. J. B. T.

Action of Alkylene Bromides on Thiamides. By S. GABRIEL and P. HEYMANN (*Ber.*, **24**, 783—788).—The authors have already (Abstr., 1890, 524) described the formation of μ-phenylthiazoline,  $C_2H_4{<}^{N}_{S}{>}CPh$, by the action of boiling ethylene bromide on thiobenzamide. They now find that a different reaction takes place when the conditions are altered.

Ethylene imidothiobenzoate hydrobromide, $C_2H_4(S{\cdot}CPh{:}NH)_2,2HBr$, is obtained as a white, granular mass by warming thiobenzamide (10 grams) with ethylene bromide (100 grams) on the water-bath and washing the product with absolute alcohol. It is easily soluble in water, melts at 233°, and, when boiled with water, is decomposed into ammonium bromide and *ethylene mercaptan dibenzoate*, $C_2H_4(SCOPh)_2$; this crystallises from alcohol in tablets and melts at 96°. The same salt is obtained by shaking ethylene mercaptan with excess of potash and benzoic chloride. A small quantity of the ethylene imidothiobenzoate is decomposed by water to yield ethylene mercaptan and benzamide.

μ-Phenylthiazoline, when warmed with bromine-water, is oxidised to benzoyltaurine; if, however, an alcoholic solution of the base is treated with a solution of bromine in alcohol, a bromo- additive compound, $C_9H_9NSBr_2$, is obtained which crystallises in large, yellow needles.

Methyl-μ-phenylthiazoline,  $\begin{matrix} CHMe{\cdot}S \\ | \\ CH_2{-}N \end{matrix}{>}CPh$, is obtained as a yellow oil, on boiling a mixture of propylene bromide and thiobenzamide. The *picrate*, $C_{10}H_{11}NS,C_6H_3N_3O_7$, is sparingly soluble. When oxidised with bromine-water, it yields a crystalline compound which on account of its great solubility could not be purified, and is probably *benzoylmethyltaurine*, $SO_3H{\cdot}C_3H_6{\cdot}NH{\cdot}COPh$. The latter, on hydrolysis in a sealed tube with hydrochloric acid at 160°, yields benzoic acid and β-methyltaurine, $NH_2{\cdot}CH_2{\cdot}CHMe{\cdot}SO_3H$.

μ-Orthotolylthiazoline,  $C_6H_4Me{\cdot}C{<}^{N}_{S}{>}C_2H_4$, is obtained by the action of ethylene bromide on orthotoluylthiamide. It is a yellow oil which decomposes when distilled at the ordinary pressure, but distils without decomposition between 200° and 203° under 90 mm. The *picrate* is obtained on adding picric acid to a solution of the hydrochloride. The *platinochloride* decomposes at 200° with frothing and a brown coloration. On oxidation with bromine-water and hydrolysis of the resulting compound, it yields taurine and orthotoluic acid.

Orthotoluylthiamide is prepared by heating orthotolunitrile with ammonium sulphide under pressure; it crystallises from water and melts at 88°.

μ-Paratolylthiazoline is prepared in a similar way to the ortho-compound; it is a white, crystalline solid, insoluble in water, crystal-

lises from hot alcohol in beautiful, indented plates, melts at 81°, and is volatile with steam.

Paratoluylthiamide is obtained from paracyanotoluene in the same way as the ortho-compound. It forms beautiful, yellow needles and melts at 168°.

No anhydro-base was obtained from ethylene bromide and thiacetamide. If a mixture of the two substances (10 : 1) is boiled, only a very small quantity of hydrogen bromide is evolved. When a mixture of equal weights is heated on the water-bath, *ethylene imidothioacetate hydrobromide*, $C_2H_4(SCMe\!:\!NH)_2,2HBr$, is formed. On boiling with water, it appears to give products similar to those obtained from the above aromatic compound. E. C. R.

Isomeric Ethyl Amidotolylcarbamates. By H. SCHIFF and A. VANNI (*Ber.*, **24**, 687—689).—By the action of ethyl chloroformate on 1 : 2 : 4-diamidotoluene (Abstr., 1890, 1124), the authors obtained an ethyl amidotolylcarbamate, $NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}COOEt$, melting at 90—91°, which, on boiling with ethyl oxalate and alcohol, was converted into *ethyl oxamethanetolylcarbamate*,

$$OEt{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}COOEt,$$

melting at 128°. If amidotolyloxamethane is treated with ethyl chloroformate, an isomeric compound is obtained, which melts at 131°, but is otherwise very similar to the first compound. By the action of alcoholic ammonia, both are converted into monamides, having the formula $NH_2{\cdot}C_2O_2{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}COOEt$. These crystallise in lustrous prisms; the one obtained from the isomeride of m. p. 128° melts at 223°, and that from the higher melting isomeride at 209°.

To ascertain the exact position of the groups in these isomerides, 1 : 2 : 4-nitrotoluidine was treated with ethyl chloroformate, and the resulting *ethyl nitrotolylcarbamate*, which crystallises in colourless needles and melts at 137°, reduced with stannous chloride and hydrochloric acid. The ethyl amidotolylcarbamate formed, crystallises in colourless prisms which become yellow in the air, and although it melts at 91°, is not identical with the ethyl amidotolylcarbamate obtained from 1 : 2 : 4-diamidotoluene. On treatment with ethyl oxalate, it forms the ethyl oxamethanetolylcarbamate melting at 131°. Hence, in the ethyl amidotolylcarbamate obtained from 1 : 2 : 4-ethyl nitrotolylcarbamate, the NH·COOEt group occupies the position 2, and the amido-group the position 4, whilst in the compound obtained from 1 : 2 : 4-diamidotoluene, these positions are reversed.

H. G. C.

Benzylidenebiuret and Chlorobenzylidenethiobiuret. By J. J. ABEL (*Amer. Chem. J.*, **13**, 114—119).—*Benzylidenebiuret*, $C_9H_9N_3O_2$, is prepared by heating carbamide (3 mols.) with benzal chloride (1 mol.) in a flask on the sand-bath until the temperature reaches 198—200°, after which the reaction is allowed to proceed without further application of heat. When the product has cooled to 100°, it is treated with boiling water, collected, washed with hot alcohol, dissolved in much hot water, and allowed to crystallise.

Ammonium chloride and cyanic acid are formed at the same time as the benzylidenebiuret.

When slowly crystallised, benzylidenebiuret forms large, glistening, rhombic prisms; otherwise, clusters of fine needles are obtained. It melts at 258° (uncorr.) with decomposition; it dissolves sparingly in phenol, hot water, and alcohol, slightly in ether and chloroform, not at all in carbon bisulphide. Its aqueous solution is precipitated by most metallic salts. When boiled with alkalis, it is decomposed into benzaldehyde, carbamide, ammonia, and carbonic anhydride. Strong sulphuric acid dissolves it, and when the solution is diluted, a compound crystallises out in large clusters of rhombic prisms. The author favours the structural formula $\mathrm{CHPh}{<}\substack{\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}}{>}\mathrm{NH}$ for benzylidenebiuret, but evidence is yet lacking. Its *platinochloride* and some of its double salts with other metallic chlorides were obtained.

Chlorobenzylidenethiobiuret, $C_9H_{10}ClS_2N_3$, is obtained by heating dry thiocarbamide (40 grams) with benzal chloride (60 grams) until action begins, at which point the heating is discontinued. The product is recrystallised from hot water and purified by precipitation from hot alcohol by the addition of ether; the new compound is thus obtained in snow-white, crystalline flakes. Ammonium chloride is the only other product, Brodsky's benzylidenethiobiuret (Abstr., 1887, 580) not being obtainable by this method. When chlorobenzylidenethiobiuret is dissolved in strong sulphuric acid or glacial acetic acid, new chlorine-free products are obtained; these, as well as the parent substance are still being investigated. A. G. B.

Production of Orthochloranisaldehyde from Paranitrotoluene. By F. Tiemann (*Ber.*, **24**, 699—713).—Paranitrometamethoxybenzaldehyde was obtained by Ulrich (Abstr., 1886, 60) by the oxidation of paranitrometamethoxycinnamic acid, and is of importance, as it should yield vanillin on substituting hydroxyl for the nitro-group; this could not, however, be definitely established on account of the difficulty of obtaining a sufficiency of the compound by Ulrich's method, which is a very complicated one, involving great loss of material.

A simpler method of preparing the nitromethoxybenzaldehyde from paranitrometachlorotoluene was, however, described by Landsberg (Abstr., 1887, 483), and this has since been reinvestigated by Riecher (Abstr., 1889, 1170), who confirmed Landsberg's results, but pointed out (*Ber.*, **22**, 2344 and 2363) that as the starting compound was in reality paranitrorthochlorotoluene (compare Lellman, Abstr., 1884, 1133), the production of the metamethoxy-derivative, when the nitrochlorobenzaldehyde (Landsberg, *loc. cit.*) is heated with sodium methoxide, involved an isomeric change. In attempting to displace the nitro-group by hydrogen, by the usual method, in the supposed nitromethoxybenzoic acid, prepared by Landsberg's method, the author found that this was scarcely acted on by ferrous hydroxide; he then discovered that it contained chlorine but not nitrogen, and finally proved it to be paramethoxyorthochlorobenzoic acid (orthochloranisic acid). It was thus evident that when the nitrochlorobenzaldehyde is heated with sodium methoxide, the nitro-group, and not the chlorine atom, is displaced by methoxyl. It is probable therefore that both Landsberg and Riecher dealt with a mixture of methoxychlorobenzaldehyde, containing unaltered nitrochloro-derivative. This is supported by the fact that the two compounds cling to each other with extreme tenacity (see below), the mixture having the same melting point as paranitrometamethoxybenzaldehyde, prepared by Ulrich's method.

Paranitrorthochlorotoluene was prepared by Wachendorff's method (compare Lellmann, *loc. cit.*). It is converted into the *nitrochlorobenzyl bromide* melting at 49—50°, when heated with bromine (1 mol.) in a sealed tube for four hours at exactly 130—135°; the latter yields *nitrochlorobenzaldehyde*, when 25 grams of it is digested in a reflux apparatus for 48 hours with a solution of lead nitrate containing 90 grams in 1500 c.c. of water; this crystallises from light petroleum in delicate, white needles, and melts at 79°.

Paranitrorthochlorobenzoic acid, melting at 138—139°, is formed when either of the three last-mentioned derivatives is oxidised with potassium permanganate. The corresponding amido-acid melts at 214·5°, and yields 1 : 2-chlorobenzoic acid, when an alcoholic solution is heated with ethyl nitrite.

Orthochloranisaldehyde is formed when paranitrorthochlorobenzaldehyde (1 mol.) is heated on the water-bath in a reflux apparatus for three hours with sodium methoxide (1 mol.) in methyl alcoholic solution; after evaporating the methyl alcohol, the product is steam-distilled. It is best separated from the unaltered nitro-derivative by repeatedly dissolving in concentrated sodium hydrogen sulphite solution, adding sodium carbonate, and steam-distilling, but although no nitrogen could be detected by qualitative tests, the compound was not obtained quite pure after eight such treatments. The analytical results indicated that the product contained 2—3 per cent. of unaltered nitro-derivative. It forms long, white needles, melts at 62—63°, and is easily soluble in alcohol, ether, benzene, and light petroleum, sparingly in water. The *oxime*, $OMe\cdot C_6H_3Cl\cdot CH{:}NOH$, crystallises from hot water in beautiful, white needles, melts at 93°, and is readily soluble in alcohol, ether, chloroform, and benzene; it is precipitated unaltered from its solutions in alkalis, on the addition of an acid. The hydrazone, $OMe\cdot C_6H_3Cl\cdot CH{:}N_2HPh$, separates from dilute alcohol in yellowish-red needles, melts at 103°, and is easily soluble in alcohol, ether, and chloroform.

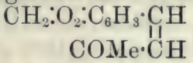
Orthochloranisic acid is prepared by oxidising the aldehyde with potassium permanganate. After repeated recrystallisations from dilute alcohol, it was obtained quite pure. It is almost insoluble in boiling water, but easily soluble in alcohol, ether, and benzene; it melts at 208°. By prolonged boiling with water and sodium amalgam, anisic acid is formed. A. R. L.

Piperonal Derivatives. By F. HABER (*Ber.*, **24**, 617—626; compare Abstr., 1890, 1140).—*Dipiperonylacryl ketone*,

$$(CH_2{:}O_2{:}C_6H_3\cdot CH{:}CH)_2CO,$$

is prepared by the action of piperonal on acetone in presence of soda at the ordinary temperature; it crystallises from alcohol in slender, yellow needles, melts at 185°, and is readily soluble in chloroform or acetone; with concentrated sulphuric acid, an intense blue coloration is formed, changing gradually to violet-red. The *phenylhydrazone* is unstable.

Dinitrodipiperonylacryl ketone, $[CH_2:O_2:C_6H_2(NO_2)\cdot CH:CH]_2CO$, is obtained by the nitration of the ketone in glacial acetic acid solution; it crystallises from acetone in yellow needles, and melts at 218° with decomposition.

Piperonylacryl methyl ketone, $CH_2:O_2:C_6H_3\cdot CH:CH\cdot COMe$, is formed from piperonal and acetone by treatment with very dilute soda; it is readily soluble in alcohol, crystallises in long, yellow, prismatic needles, and melts at 107°. When the substance is heated in a current of steam, or when fractionally recrystallised from water, a compound is obtained which is regarded as a stereometric isomeride of *isopiperonylacryl methyl ketone*, 
$\begin{array}{r} CH_2:O_2:C_6H_3\cdot CH \\ \| \\ COMe\cdot CH \end{array}$; it is more soluble than the previous modification, crystallises in small, white, slender needles, and melts at 111°; when heated at 190°, it is converted into the isomeride of lower melting point. The normal *phenylhydrazone*, $CH_2:O_2:C_6H_3\cdot CH:CH\cdot CMe:N_2HPh$, is deposited from alcohol in yellow crystals melting at 158—160° with decomposition. The corresponding *iso-derivative* crystallises in small, white needles, and melts at 163°. The *normal oxime*, $CH_2:O_2:C_6H_3\cdot CH:CH\cdot CMe:NOH$, is obtained in small, pale-yellow crystals melting at 186°; it could not be converted into a β-modification, and is readily decomposed by the action of dehydrating agents. The *iso-oxime* is white, and melts at 183°.

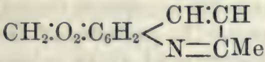
Orthonitropiperonylacryl methyl ketone,

$$CH_2:O_2:C_6H_2(NO_2)\cdot CH:CH\cdot COMe,$$

prepared by treatment of the ketone with nitric acid, crystallises from acetone in yellow needles, and melts at 153°. Attempts to convert the compound into an indigo derivative were unsuccessful.

The *phenylhydrazone*, $CH_2:O_2:C_6H_2(NO_2)\cdot CH:CH\cdot CMe:N_2HPh$, crystallises from alcohol in red needles, and melts at 197°; on account of the colour of this substance, it is perhaps better represented by the tautomeric azo-formula

$$CH_2:O_2:C_6H_2(NO_2):CH:CH\cdot CHMe\cdot N_2\cdot Ph.$$

Dioxymethylenequinaldine, 
$CH_2:O_2:C_6H_2{<}\begin{array}{l} CH:CH \\ \quad\;\, | \\ N{=}CMe \end{array}$, is formed by the reduction of the nitro-ketone with tin and hydrochloric acid, or with ferrous sulphate and ammonia; it crystallises from water in colourless needles, and melts at 152°; the yield is very small. The *chloride* and *sulphate* are readily soluble; the *picrate* melts at 175°; the *platinochloride* is pale-grey; the *chromate* crystallises in small, yellow needles, and melts at 210° with decomposition.

By the nitration of piperonal below 6°, the ortho-derivative is obtained, but above this temperature a mixture of ortho- and meta-nitropiperonal is formed.

Orthonitropiperonalphenylhydrazone, $CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CH{:}N_2HPh$, crystallises in red needles melting at 212°. The *oxime*,

$$CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CH{:}NOH,$$

is deposited from alcohol in yellow needles, and melts at 203°. *Orthonitropiperonylnitrile*, $CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CN$, is formed on heating the oxime with acetic anhydride, and melts at 138—139°.

Orthamidopiperonaloxime, $CH_2{:}O_2{:}C_6H_2(NH_2)\cdot CH{:}NOH$, is prepared by the reduction of the nitro-derivative with hydrogen sulphide, and is deposited in yellow, crystalline scales melting at 175·5°; a red coloration is produced with concentrated sulphuric acid. Orthonitropiperonal cannot be readily reduced.

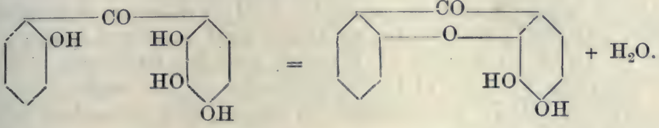
Orthacetoamidopiperonylnitrile, $CH_2{:}O_2{:}C_6H_2(CN)\cdot NHAc$, is formed when the amidoxime is boiled with acetic anhydride and sodium acetate; it crystallises from alcohol in yellow needles, and melts at 216°. By heating the oxime with acetic anhydride alone, *diacetylorthamidopiperonaloxime*, $CH_2{:}O_2{:}C_6H_2(NHAc)\cdot CH{:}NOAc$, is formed; it crystallises in yellow-grey aggregates, melts at 188°, and is not acted on by sodium acetate and acetic anhydride.

J. B. T.

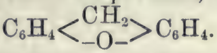
Hydroxyketone Dyes. A New Dihydroxyxanthone. By C. Graebe and A. Eichengrün (*Ber.*, **24**, 967—970).—It has been found that the presence of a single carbonyl group is in many cases sufficient to cause an aromatic compound to show tinctorial properties, as, for example, the various hydroxybenzophenones. In order to compare the relationship of these compounds to the anthraquinone-derivatives, and to the euxanthone group, the authors have examined the trihydroxybenzophenone obtained from benzoic acid and pyrogallol, known in commerce as alizarin-yellow, the tetrahydroxybenzophenone from salicylic acid and pyrogallol, and the tetrahydroxyphenylnaphthyl ketone from gallic acid and naphthol (alizarin W). They have been able to confirm the formulæ already given, and find that all readily yield oximes and hydrazones. The salts containing only one equivalent of metal are the most readily prepared, and it is very difficult to displace all the hydrogen of the hydroxyl groups by methyl or ethyl. Thus trihydroxybenzophenone yields, according to circumstances, either a mono- or a di-methoxy-derivative. The latter is only soluble with difficulty in soda solution, but yields a crystalline acetyl derivative, $COPh\cdot C_6H_2(OMe)_2\cdot OAc$, conclusively showing the presence of three hydroxyl groups.

Another characteristic of these substances is their behaviour with sulphuric acid. Tri- and tetra-hydroxybenzophenone are converted into pyrogallolsulphonic acid and benzoic or salicylic acid. As regards the position of the hydroxyl groups in the trihydroxy-compound, two different formulæ, [Bz : OH : OH : OH = 1 : 2 : 3 : 4; or 1 : 3 : 4 : 5], are possible. The former supposition is regarded as more probable, inasmuch as in the tetrahydroxy-compound obtained from salicylic acid and pyrogallol, the hydroxyl groups, as will be shown below, must occupy the positions 2 : 3 : 4.

When tetrahydroxybenzophenone is heated with water at 180—220°, it is converted into a new dihydroxyxanthone (compare Abstr., 1890, 504). This reaction can only take place in the following manner:—



The hydroxyl groups must therefore occupy the positions 2 : 3 : 4.

3 : 4-*Dihydroxyxanthone* is obtained from its alkaline solution in pale-yellow, microscopic needles, and crystallises from alcohol likewise in pale-yellow needles containing 3 mols. H_2O. Like euxanthone, it melts at 240°, and sublimes, although somewhat less readily, in pale-yellow needles. Its alkaline solutions are blood-red, and it dyes cotton mordanted with alumina a yellow colour. It is sparingly soluble in water, readily in alcohol, and yields a *diacetyl* compound, $C_{13}H_6O_2(OAc)_2$, melting at 161°. When heated with zinc-dust, it only yields small quantities of a reduction product, which appears to be diphenylenemethane oxide,  $C_6H_4{<}\substack{CH_2\\ -O-}{>}C_6H_4$. On treatment with bromine, it yields two derivatives having the composition $C_{13}H_7O_4Br$ and $C_{13}H_5O_4Br_3$. H. G. C.

Ethereal Salts of Chlorhydrins. By C. GÖTTIG (*Ber.*, **24**, 508—510).—Berthelot has shown (*Ann. Chim. Phys.* [3], **41**, 216) that when hydrogen chloride is passed into heated mixtures of glycerol with acids, the corresponding glycerol ether may in certain cases be obtained. The author finds that at a higher temperature ethereal salts of the chlorhydrins may be obtained, and has prepared and examined the salicylate of dichlorhydrin, $OH\cdot C_6H_4\cdot COO\cdot C_3H_5Cl_2$. It is formed by treating a saturated solution of salicylic acid in glycerol at 108° with hydrogen chloride for nine hours, the separated oil crystallising for the most part on cooling. Dichlorhydrin salicylate crystallises from alcohol in white, prismatic crystals, melts at 44°, has a sp. gr. of 1·331, and is readily soluble in alcohol, ether, chloroform, and benzene, scarcely in water. The empirical formula also agrees with the constitution $C_6H_4Cl\cdot CO\cdot OC_3H_5Cl\cdot OH$, but the ether only yields salicylic acid on hydrolysis, and no trace of orthochlorobenzoic acid, and by the action of alkalis at 100° yields much epichlorhydrin. As the latter is only obtained from dichlorhydrins, and not from monochlorhydrins, the formula first given must be correct. H. G. C.

Salts of Dichlorhydrin with Aromatic Acids. By P. FRITSCH (*Ber.*, **24**, 775—778).—Berthelot has shown that the product obtained by the action of hydrogen chloride on a mixture of glycerol and benzoic acid is benzochlorhydrin; and Maxwell Simpson obtained glycolchloracetin by treating a mixture of glycol and glacial acetic acid with hydrogen chloride at 100°, and glycolchlorobenzoicin from glycol and benzoic acid. On the other hand, Göttig obtained the monoglyceride of salicylic acid from glycerol and salicylic acid, under what appear to be similar conditions. The author obtains only the dichlorhydrin salt of the aromatic acid when hydrogen chloride is passed into a mixture of glycerol and an aromatic acid as long as it is absorbed. Benzoic, salicylic, paracresotic, or anisic acid is mixed with an equal weight to twice its weight of glycerol, and dry hydrogen chloride is passed into the mixture at the temperature of the water-bath. The dichlorhydrin salt is precipitated as an oil, and is washed with hot water and dilute soda.

Benzodichlorhydrin boils at 230—235° under 150 mm., has the specific gravity 1·28 at 15°, is a thick oil which does not crystallise, and is insoluble in water.

The dichlorhydrin salts of salicylic, paracresotic, and anisic acids are insoluble in water, solidify when cooled, and may be purified by crystallisation from alcohol, in which they are easily soluble. *Salicyldichlorhydrin* crystallises in long needles and melts at 45°. *Paracresotodichlorhydrin* crystallises in slender needles and melts at 45·5°. *Anisodichlorhydrin* crystallises in lustrous scales and melts at 81°.

The author assumes these compounds to have the constitution represented by the formula $OX{\cdot}CH(CH_2Cl)_2$ (X being an acid radicle, Bz,Ac). Reboul has shown that dichlorhydrin and acetodichlorhydrin are formed by the action of hydrogen chloride on a mixture of glycerol and glacial acetic acid, and Markovnikoff by the same method obtained the dichlorhydrin $CH_2Cl{\cdot}CH(OH)CH_2Cl$, its formation being due to the action of hydrogen chloride on the acetate $OAc{\cdot}CH(CH_2{\cdot}OH)_2$. E. C. R.

Triglycerides of Aromatic Acids. By P. FRITSCH (*Ber.*, **24**, 779—782).—The salts of dichlorhydrin with aromatic acids, described in the preceding abstract, are easily converted into simple and mixed triglycerides. The dichlorhydrin salt (1 mol.) is heated with somewhat more than 2 mols. of the sodium or potassium salt of the aromatic acid for some hours at 180—200°. After washing out the metallic chloride with water, the triglyceride is obtained as an oil. The triglycerides of aromatic acids can mostly be obtained crystalline from ethereal solution, and are best purified by washing the crystals so obtained with alcohol and recrystallising from ether or methyl alcohol. *Tribenzoïn*, melting at 70·5°, crystallises in concentrically-grouped needles of silky lustre. *Trisalicylin* melts at 79° and crystallises in lustrous needles. *Trianisin* melts at 103·5° and crystallises in needles. *Triparacresotin* melts at 118° and is a crystalline, friable mass. *Disalicylbenzoïn* melts at 95° and crystallises in needles. *Dibenzosalicylin* is an oil. The triglycerides of the aromatic acids, like the natural fats, are insoluble in water, sparingly soluble in alcohol, and easily soluble in ether, chloroform, benzene, and carbon bisulphide. E. C. R.

Action of Chlorine on Hydroxybenzoic Acids. By T. ZINCKE and H. WALBAUM (*Annalen*, **261**, 208—254).—*Hexachlorometaketotetrahydrobenzoic acid*, $C_7H_2Cl_6O_3$, is gradually deposited in crystals when a glacial acetic acid solution of metahydroxybenzoic acid is kept, saturated with chlorine, for six to seven days at the ordinary temperature. It crystallises from glacial acetic acid, and from a mixture of ether and light petroleum, in colourless, well-defined plates, turns yellow at 180°, and melts at about 190° with decomposition; it is readily soluble in alcohol, ether, and hot glacial acetic acid, but more sparingly in benzene and light petroleum, and almost insoluble in water and dilute hydrochloric acid; the salts of the acid could not be obtained. It is decomposed by boiling water, the solution giving off an odour of chlorophenols. When boiled with alcohol, it is converted into tetrachlorometahydroxybenzoic acid, and, when treated with potassium iodide or stannous chloride, it is converted into trichlorometahydroxybenzoic acid. It dissolves slowly in sodium carbonate, yielding a brownish-yellow solution, from which it is, for the most part, precipitated unchanged on acidifying immediately; if, however, the alkaline solution is kept for some time, no precipitate is produced on the addition of an acid. It is quickly decomposed by ice-cold, 50 per cent. potash, yielding a crystalline acid, which has not yet been obtained in a pure condition, and which, when boiled with water, is converted into a more stable acid, with evolution of carbonic anhydride.

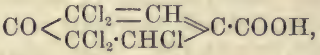
Trichlorometahydroxybenzoic acid, $C_7H_3Cl_3O_3 + H_2O$ [$Cl_3 = 1:3:5$], can be prepared by passing chlorine into a solution of metahydroxybenzoic acid in glacial acetic acid until the solution smells of the gas, and then allowing it to evaporate; the product is deposited in colourless prisms, and can be purified by recrystallisation from hot hydrochloric acid. It forms colourless plates or needles, which contain 1 mol. H_2O and melt at 104—105°; on further heating, the water of crystallisation is expelled, the anhydrous compound melting at 143—144°. It is very readily soluble in alcohol, ether, hot glacial acetic acid, and benzene, but only sparingly in water; it is not acted on by stannous chloride, even at 100°; when treated with chlorine, it is converted into the hexachlorinated acid described above, and, on distillation with lime, it yields symmetrical trichlorophenol (m. p. 67—68°). The *silver* salt, $C_7H_2Cl_3O_3Ag$, is a colourless, crystalline powder. The *methyl* salt, $C_8H_5Cl_3O_3$, can be prepared by treating the silver salt with methyl iodide; it crystallises from hot light petroleum in colourless needles or prisms, melts at 90°, and is readily soluble in alcohol, ether, and benzene. The *acetyl* derivative, $OAc{\cdot}C_6HCl_3{\cdot}COOMe$, prepared by heating the methyl salt with acetic chloride, crystallises in lustrous, well-defined plates, melts at 65°, and is readily soluble in benzene, alcohol, and light petroleum.

Tetrachlorometahydroxybenzoic acid, $C_7H_2Cl_4O_3$, is deposited in crystals when a solution of the hexachlorinated acid in absolute alcohol (5 parts) is boiled for three to four hours, then mixed with dilute (1 : 10) hydrochloric acid (3 mols.), and allowed to evaporate. It crystallises from hot dilute hydrochloric acid in colourless needles or prisms, melts at 170—172°, distils with only slight decomposition, and is readily soluble in ether, alcohol, and glacial acetic acid, and moderately easily in hot benzene and dilute hydrochloric acid; it is not acted on by boiling concentrated nitric acid, but when treated with chlorine in glacial acetic acid solution it yields a keto-chloride, C_6Cl_8O (m. p. 105—106°), identical with the compound obtained by Benedikt and Schmidt (*Monatsh.*, **4**, 607), by treating pentachlorophenol with chlorine; on distillation with lime, it gives the tetrachlorophenol described below. The *barium* salt, $(C_7Cl_4O_3)_2Ba$, is a colourless, crystalline powder, very readily soluble in water. The *silver* salt, $OAg\cdot C_6Cl_4\cdot COOAg$, is insoluble in water and alcohol. The *methyl* salt, $OMe\cdot C_6Cl_4\cdot COOMe$, prepared from the silver salt, crystallises from light petroleum in colourless needles, melts at 37—38°, and is readily soluble in the ordinary solvents.

Acetyltetrachlorometahydroxybenzoic acid, $OAc\cdot C_6Cl_4\cdot COOH$, is obtained when the acid is heated with acetic chloride at 100°; it crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 150—151°, and is readily soluble in alcohol and hot benzene, but almost insoluble in light petroleum. The *silver* salt, $OAc\cdot C_6Cl_4\cdot COOAg$, prepared from the ammonium salt, is a colourless, granular compound. The *methyl* salt, $OAc\cdot C_6Cl_4\cdot COOMe$, crystallises in small, colourless needles, melts at 68—69°, and is readily soluble in alcohol, ether, and benzene, but more sparingly in light petroleum.

Tetrachlorophenol, $[OH : Cl_4 = 1 : 2 : 3 : 4 : 6]$, is obtained in small quantities when the tetrachlorinated acid is carefully distilled with soda-lime in an atmosphere of hydrogen. It crystallises from light petroleum in small, colourless needles, melts at 67°, and is readily soluble in most ordinary solvents, except water. The *benzoyl* derivative, $C_6HCl_4\cdot OBz$, is formed when the phenol is heated with benzoic anhydride; it separates from alcohol and light petroleum in small, colourless prisms melting at 113—115°.

Pentachloroparaketotetrahydrobenzoic acid,



$$\mathrm{CO}<\begin{matrix}\mathrm{CCl_2{=}CH}\\ \mathrm{CCl_2\cdot CHCl}\end{matrix}>\mathrm{C\cdot COOH},$$

is obtained by passing chlorine into a hot glacial acetic acid solution of parahydroxybenzoic acid until no separation of crystals of the dichloro-derivative occurs on cooling a portion of the solution; the liquid is then saturated at the ordinary temperature, kept for some days, and then allowed to evaporate, when the acid is obtained in colourless crystals. It melts at 180—181°, decomposes at about 200°, and is readily soluble in alcohol, ether, glacial acetic acid, and hot benzene, but almost insoluble in light petroleum; when treated with stannous chloride or potassium iodide, it is converted into dichloroparahydroxybenzoic acid. It is quickly decomposed by alkalis and by boiling water, but it undergoes no change on boiling with alcohol.

Dichloroparahydroxybenzoic acid, identical with the compound obtained by Lössner (*J. pr. Chem.* [2], **13**, 434) by heating parahydroxybenzoic acid with antimony pentachloride, is deposited in crystals when chlorine is passed into a cold glacial acetic acid solution of parahydroxybenzoic acid; it melts at 259—260°, is not acted on by stannous chloride, and yields dichlorophenol $[OH : Cl_2 = 1 : 2 : 6]$, on distillation with lime. The *methyl* salt, $C_8H_6Cl_2O_3$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises in colourless needles, melts at 121—122°, and dissolves freely in alcohol, ether, &c. The *acetyl* derivative, $OAc\cdot C_6H_2Cl_2\cdot COOMe$, obtained by treating the methyl salt with acetic chloride, crystallises from methyl alcohol in colourless plates melting at 68—69°.

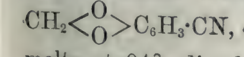
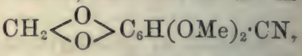
Dichlorosalicylic acid can be obtained by passing chlorine into a solution of salicylic acid in glacial acetic acid; it crystallises in colourless prisms, melts at 219°, and yields dichlorophenol [$OH : Cl_2 = 1 : 2 : 4$], on distillation with lime. The methyl salt melts at 143—144°. The *acetyl* derivative, $OAc\cdot C_6H_2Cl_2\cdot COOMe$, crystallises from alcohol in colourless needles, and melts at 57°. F. S. K.

Action of Phenylhydrazine and Hydroxylamine on some Ketonic Acids. By F. GARELLI (*Gazzetta*, **20**, 692—701).—*Paramethoxyphenylglyoxylic acid*, $OMe\cdot C_6H_4\cdot CO\cdot COOH$, is formed, together with anisic acid, when anethoïl is oxidised with potassium permanganate, and is analogous to the ketonic acids obtained by Ciamician and Silber (Abstr., 1890, 965) from isosafrole, isomethyleugenol, and isoapiole, forming the lowest member of this series of substituted hydroxyphenylglyoxylic acids. When pure, it crystallises from boiling benzene in needles melting at 89°, and from water in hydrated needles which melt at 60°; it dissolves in hot benzene, and very freely in alcohol, ether, and acetic acid. The yield is 40 per cent. The *hydrazone*, $C_{15}H_{14}O_3N_2$, obtained by treating the aqueous solution of the acid with phenylhydrazine hydrochloride, crystallises from benzene in minute prisms; it is insoluble in water, but freely soluble in alcohol, ether, and also in sodium carbonate; from the latter solution, it is reprecipitated unchanged on acidification.

The *hydrazone* of *dioxymethylenephenylglyoxylic acid* (from isosafrole), $C_{15}H_{12}O_4N_2$, is decomposed on repeated crystallisation from hot benzene. From its solution in sodium carbonate it is precipitated by hydrochloric acid as a yellow, amorphous powder which melts at 149°, and dissolves in all ordinary solvents except water.

The *hydrazone* of *dimethoxyphenylglyoxylic acid* (from isomethyleugenol), $C_{16}H_{16}O_4N_2$, is an unstable compound, obtained like the previous substance as a clear, yellow powder which melts at 179°, and is insoluble in water, but dissolves in alcohol, ether, and hot benzene.

The *hydrazone* of *apionylglyoxylic acid*, $C_{17}H_{16}O_6N_2$, is even more unstable than the preceding compounds, and is altered by exposure to light. It is obtained as a pale-yellow powder, melts at 169—170°, and dissolves in all ordinary solvents except water.

The above ketonic acids do not yield oximes on treatment with hydroxylamine hydrochloride, the products of the action of this reagent on the hot aqueous solution of the acids being more or less volatile compounds, insoluble in sodium carbonate and potash, and having a characteristic odour. They are regarded by the author as nitriles formed by the simultaneous elimination of water and carbonic anhydride from the oximes. *Piperonylnitrile*,  $CH_2<\substack{O\\O}>C_6H_3\cdot CN$, crystallises from water in slender, white needles, melts at 94°, dissolves sparingly in water, freely in alcohol, ether, benzene, &c., and not at all in sodium carbonate and potash. It has a pungent, but not disagreeable odour, and readily volatilises in steam. Anisonitrile, $OMe\cdot C_6H_4\cdot CN$, crystallises in white needles, melts at 57—58°, and has a sweet, penetrating odour; it readily dissolves in alcohol, ether, &c., but only very sparingly in water, and not at all in sodium carbonate and potash. It is thus identical with the anisonitrile described by Henry (*Ber.*, **2**, 667), and by Miller (Abstr., 1890, 144). *Veratronitrile*, $(OMe)_2C_6H_3\cdot CN$, crystallises from water in small, shining needles. It is less volatile than the preceding compound, and has a less marked odour. It melts at 67—68°, dissolves readily in ordinary solvents, sparingly in water, and not at all in potash or sodium carbonate. *Apionitrile*,  $CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H(OMe)_2\cdot CN$, may be crystallised from dilute alcohol; it is very slightly volatile, and has only a feeble odour. It is quite insoluble in water, but dissolves in other solvents. It melts at 135·5°. S. B. A. A.

Action of Sodium Phenylmercaptide on Ethyl Chloracetoacetate. By R. Otto and A. Rössing (*Ber.*, **24**, 685—687).—The action of sodium phenylmercaptide on ethyl chloracetoacetate has been examined by Autenrieth (this vol., p. 540), who obtained phenyl bisulphide as the sole product under very varying conditions. The authors have repeated the experiment, and find that when equivalent quantities of the two substances are mixed in alcoholic solution, boiled for an hour, the alcohol evaporated off at a low temperature, and the residue mixed with water, an oil is obtained, which, even on the addition of a crystal of phenyl bisulphide, does not solidify, and has only a feeble odour. It appears to be ethyl thiophenylacetoacetate mixed with a little phenyl bisulphide. H. G. C.

Action of Ethyl Sodacetoacetate on Ethyl Benzalmalonate. By J. Bredt (*Ber.*, **24**, 603—605).—By the action of ethyl sodacetoacetate and ethyl benzylmalonate in molecular proportion in alcoholic solution at 0°, a crystalline *sodium salt* is slowly deposited; it is not decomposed by carbonic anhydride, but on treatment with mineral acids, a compound of the formula $C_{18}H_{20}O_6$ is precipitated; this is very sparingly soluble in water, but dissolves in alcohol, and is deposited in crystalline aggregates; it melts at 155° with decomposition. The *silver salt* is also crystalline. J. B. T.

Ethyl Hydrogen Hemipinate. By R. Wegscheider (*Monatsh.*, **11**, 538—544).—This salt, $COOH\cdot C_6H_2(OMe)_2\cdot COOEt$, has been prepared by the following methods:—(1.) From hemipinic acid (obtained from narcotine), by the action of hydrogen chloride on a solution in 10—15 times its weight of alcohol, and subsequent recrystallisation of the product from water, or treatment of it with dilute aqueous potash and reprecipitation by means of a dilute acid. (2.) From hemipinic acid, by first converting it into the corresponding anhydride and boiling this for several hours with absolute alcohol in a reflux apparatus. (3.) From diethyl hemipinate, $C_{10}H_8O_6Et_2$ (m. p. 70—72°), by heating with alcoholic potash in molecular proportion. The product, in every case, melted at 148°, that is, 6° higher than the melting point previously attributed to it. The observation of Schmidt and Schilbach (*Arch. Pharm.* [3], **25**, 176), that after long-continued drying at 100°, the melting point becomes lowered to 132·5°, was not confirmed; but when the salt had been once melted in a capillary tube, the melting point fell to about 125°, a behaviour probably dependent on the partial conversion of ethyl hydrogen hemipinate into hemipinic anhydride. Ethyl hydrogen hemipinate may be obtained crystallised in the anhydrous state, or with 1 mol. H_2O, as well as in the form of the previously-described hydrated salt containing $1\frac{1}{2}$ mols. H_2O.

G. T. M.

Oxidation of Gallic Acid. By C. Boettinger (*Annalen*, **260**, 337—348; compare Abstr., 1890, 1130).—Various acids are obtained when gallic acid is oxidised with an alkaline solution of copper sulphate; the products are isolated in the following manner:—To a solution of copper sulphate (1·5 kilos.) and gallic acid (150 grams) in boiling water (4 litres), caustic soda, of sp. gr. 1·28 (1800 c.c.), is added, with constant stirring, and the mixture then boiled for half an hour; after filtering from the red precipitate which is produced, the residue is washed with water, the filtrate and washings concentrated by evaporation, acidified with sulphuric acid, and partially distilled. The distillate contains acetic acid and small quantities of an acid, probably pyruvic acid, which combines with phenylhydrazine; the residual solution is allowed to cool, separated from the crystals of sodium sulphate, the acid extracted with ethyl acetate, dissolved in water, and the diluted aqueous solution neutralised in the cold with calcium carbonate and calcium hydroxide, and filtered. The residue contains calcium oxalate and the calcium salt of an acid which the author names galic acid.

Galic acid can be easily separated from oxalic acid, as it is insoluble in dilute hydrochloric acid and only very sparingly soluble in cold water, but it dissolves freely in hot water, yielding a brown solution; it is readily soluble in alcohol and acetic acid, but insoluble in ether and chloroform. It is decomposed on heating, is converted into an acetyl derivative by boiling acetic anhydride, and dissolves in concentrated nitric acid, yielding a reddish-brown solution, from which oxalic acid is deposited on keeping for several weeks. When dried over sulphuric acid, it seems to have the composition $C_{14}H_{12}O_{13}$ (or $C_{14}H_{14}O_{13}$), but when heated at 170° it loses 2 mols. H_2O, 1 mol. being driven off at 100°. The *lead* salt, prepared by precipitating a solution of the acid with lead acetate, has probably the composition $(C_{14}H_9O_{12})_2Pb_3 + 3\frac{1}{2}H_2O$. The *barium* salt, obtained by precipitating a solution of the ammonium salt with barium chloride, is insoluble in water, and seems to have the composition $(C_{14}H_9O_{12})_2Ba_3 + 2H_2O$.

When the acid is treated with bromine in well cooled, aqueous solution, it is converted into a brown substance, which decomposes at 95°, and seems to have the composition $C_{14}H_8Br_2O_{12} + 4H_2O$; when excess of bromine is employed, and the reaction is carried out at the ordinary temperature, a yellow substance, seemingly a tetrabromide, is obtained. Hydroxylamine converts galic acid into a nitrogenous compound, which is decomposed by boiling alkali with evolution of ammonia, and phenylhydrazine transforms it into a brown substance, which is insoluble in water.

When the filtrate containing the soluble calcium salts (see above) is evaporated to dryness, the residue decomposed with sulphuric acid, and the filtered solution extracted with ether, a deliquescent acid, having the composition $C_4H_4O_3$, is obtained; on distillation, it yields pyruvic acid and compounds which reduce ammoniacal silver nitrate solution. The *calcium* salt, $(C_4H_3O_3)_2Ca$, exists in two modifications; the one contains $2\frac{1}{2}$ mols. H_2O, and is insoluble in water, the other 2 mols. H_2O, and is readily soluble. The *barium* salt, $(C_4H_3O_3)_2Ba + 1\frac{1}{2}H_2O$, is soluble in water, but is precipitated from its aqueous solution on boiling. When a solution of the acid is warmed with phenylhydrazine, a reddish-yellow hydrazone is deposited; this compound is precipitated in crystals on adding water to its solution in boiling 10 per cent. acetic acid. F. S. K.

Aromatic Sulphines. By A. MICHAELIS and E. GODCHAUX (*Ber.*, **24**, 757—764; compare Abstr., 1890, 610; 1891, 74).—The authors have not succeeded in preparing thionyldimethylaniline from dimethylaniline and thionyl chloride in the presence of aluminium chloride.

Hexamethyltriamidotriphenylsulphine chloride, $S(C_6H_4Me_2)_3Cl,6H_2O$, is prepared by dissolving mercury dimethylaniline (Schenk and Michaelis, Abstr., 1888, 834) (10 grams) in benzene (200—250 c.c.), and adding, by degrees, thionyl chloride (1·5—2 grams) dissolved in benzene (30 c.c.) to the lukewarm solution, shaking meanwhile; a voluminous, yellow precipitate separates, which subsequently assumes a red or brown colour, and, finally, becomes green in the presence of excess of thionyl chloride. It is collected, air-dried, washed with water, and boiled with moderately concentrated hydrochloric acid, until, with the exception of a small quantity of yellow powder, it is dissolved. The mercury is then removed by a current of hydrogen sulphide, and on adding sodium hydroxide to the filtrate, the sulphine chloride is precipitated together with dimethylaniline. After washing the precipitate with a little water, it is dissolved in warm alcohol, and carbonic anhydride passed through the solution to precipitate any sodium as carbonate, a little water is then added, and the solution boiled to remove the dimethylaniline; on concentrating the solution and treating with animal charcoal, the sulphine chloride separates in colourless, glistening needles; it forms thick, yellow crystals, a centimetre in length, and is obtained pure by extraction from the aqueous solution with chloroform. It is very easily soluble in alcohol and chloroform, readily in hot water, but only sparingly in ether, light petroleum, and cold water; the hydrated compound melts in its water of crystallisation at 98°, resolidifies at 120°, and the anhydrous substance then melts at 150°; it dissolves in acids. By the action of metallic sodium on an alcoholic solution of the sulphine chloride, or when its solution in hydrochloric acid is saturated with hydrogen sulphide and heated at 100° in a sealed tube, thiodimethylaniline and dimethylaniline are formed. The *platinochloride*, $(C_{24}H_{30}N_3S)_2PtCl_6$, is a flocculent, yellowish-brown precipitate, which melts at 190° with deflagration; the *mercurochloride*,

$$C_{24}H_{30}N_3SCl,HgCl_2,$$

is a dense, white precipitate which melts at 220°; whilst the *picrate*, $C_{24}H_{30}N_3SCl,C_6H_3N_3O_7$, crystallises from alcohol in quadratic plates, sparingly soluble in cold alcohol, and melts at 135°.

Hexamethyltriamidotriphenylsulphine hydroxide,

$$S(C_6H_4{\cdot}NMe_2)_3{\cdot}OH + 7H_2O,$$

is prepared by shaking a lukewarm solution of the sulphine chloride with moist silver oxide, evaporating the filtered solution to dryness, adding water, and concentrating to a small volume. It forms delicate yellow needles, and is easily soluble in water; its solutions have an alkaline reaction, but do not absorb carbonic anhydride from the air; the hydrated compound melts at 80—90°, and the anhydrous at 200°. The *bromide*, $C_{24}H_{30}N_3SBr$, is precipitated in small, delicate, white needles, by carefully neutralising a solution of the hydroxide with hydrobromic acid; it is sparingly soluble in cold water, readily in alcohol and chloroform, but insoluble in ether, and melts at 240°. The *iodide*, $C_{24}H_{30}N_3SI$, separates from alcohol in small, glittering crystals, melts at 242°, and is not very soluble in hot water, sparingly in cold alcohol, readily in hot alcohol and chloroform, but insoluble in ether.

The authors believe that the sulphur in the above derivatives is in the quadrivalent condition, but, despite their apparent analogy with compounds of quadrivalent carbon, a comparison shows that their chemical and physical behaviour is quite different. For example, hexamethyltriamidotriphenylsulphine hydroxide corresponds with hexamethyltriamidotriphenylcarbinol; but whereas the former, on treatment with hydrochloric acid, yields the colourless sulphine chloride, the latter yields the intensely coloured methyl-violet; thionylbenzene does not react with phenylhydrazine, thus differing from benzophenone.

Chlorothiobenzene, $SPh{\cdot}C_6H_4Cl$, is obtained as a heavy, colourless oil, boiling at 305—315°, together with a small quantity of a compound melting at 88° (probably dichlorothiobenzene, Kraft, this Journal, 1875, 153), when thionylbenzene and phosphorus pentachloride are brought together in molecular proportion. A. R. L.

Thionylamines. By A. Michaelis (*Ber.*, **24**, 745—757).—Thionylaniline, $C_6H_5N{:}SO$, already described by Michaelis and Herz (this vol., p. 310), is best prepared as follows:—Finely powdered aniline hydrochloride (100 grams) is suspended in dry benzene (200 c.c.), and boiled in a reflux apparatus with thionyl chloride (100 grams) until the evolution of hydrogen chloride has ceased; it is then isolated by distillation as previously described; the deposition on the condenser of a small quantity of aniline sulphite, produced by the action of moisture on the thionylaniline, indicates that the thionyl radicle is in combination with the nitrogen atom. Thionylaniline dissolves unchanged in alcohol, but when heated with it in a sealed tube at 150°, it is decomposed with the formation of hydrogen sulphide.

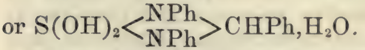
With concentrated hydrochloric acid, it reacts violently, forming aniline hydrochloride and sulphurous anhydride; it unites with dry hydrogen chloride at the ordinary temperature, but more readily when cooled by ice and salt, forming an unstable compound, $SO\!:\!NPh,2HCl$, which, however, splits up into thionyl chloride and aniline hydrochloride when treated with an excess of the acid.

Thionyl bromide, $SOBr_2$, which cannot be prepared in the same way as the chloride, is formed together with the hydrobromide of the tribromaniline melting at 118—120°, in accordance with the equation $C_6H_5\cdot N\!:\!SO + 3Br_2 = C_6H_2Br_3\cdot NH_3Br + SOBr_2$, when thionylaniline (50 grams) is dissolved in several times its volume of light petroleum, and bromine (173 grams) gradually (during several days) run in. The precipitated tribromaniline hydrobromide is then filtered off, and after distilling off the petroleum, the thionyl bromide passes over between 130° and 140° as a brown liquid, the greater portion of which boils at 136°, on repeating the distillation. As it boils with partial decomposition into sulphur bromide, bromine and sulphurous anhydride, it was not obtained quite pure and devoid of colour; it appeared to contain free bromine, and although it could be decolorised by shaking with mercury, it was then decomposed.

Thionylaniline, although analogous to phenyl isocyanate, does not combine with aniline as readily as the latter; for example, a mixture of thionylaniline and aniline only reacts if heated in a sealed tube at 200°, a colouring matter containing sulphur being formed; whilst when water or moist ether is added to a mixture of the two in molecular proportion, Schiff's aniline sulphite (*Annalen*, **140**, 125) is produced with the development of heat. The aniline sulphite described by Boessneck (Abstr., 1888, 943) is analogous to phenylcarbamic acid, and probably has the constitution, $NHPh\cdot SO\cdot OH$, Schiff's compound (*loc. cit.*) being the aniline salt of the former, $NHPh\cdot SO\cdot ONH_3Ph$; or $S(OH)_2(NHPh)_2$.

Benzaniline sulphite is prepared by dissolving thionylaniline and aniline in molecular proportion in alcohol and adding benzaldehyde. The mixture becomes warm, and the precipitated compound is collected and crystallised from alcohol. The water contained in the alcohol employed in the preparation of the compound completes the reaction, for if the above-described mixture is dissolved in an anhydrous solvent half the thionylaniline remains unaltered, and benzylideneaniline, $CHPh\!:\!NPh$, together with benzaniline sulphite, is obtained. Benzaniline sulphite forms a felt-like mass of delicate, white needles, melts at 124°, and decomposes with evolution of sulphurous anhydride at a higher temperature; it is soluble in hot alcohol and water, but only sparingly in ether, and may be kept without decomposing; it is identical with a compound described by Schiff (*Annalen*, **140**, 130; **210**, 128), and may have one of the three formulæ

$$OH\cdot CHPh\cdot NPh\cdot SO\cdot O\cdot NH_3Ph;\ OH\cdot CHPh\cdot NPh\cdot S(OH)_2\cdot NHPh;$$



$$\text{or } S(OH)_2{<}\genfrac{}{}{0pt}{}{NPh}{NPh}{>}CHPh,H_2O.$$

When thionylaniline and phenylhydrazine are mixed, a violent reaction ensues, and resinous substances, difficult to purify, are formed, but when the former is shaken with an aqueous or alcoholic solution of phenylhydrazine acetate, *thionylphenylhydrazone*, $NHPh{\cdot}N{:}SO$, and aniline acetate are formed. The hydrazone separates as a yellow compound after a short time, and is purified by crystallisation from alcohol. Similar compounds are obtained with other hydrazines and thionylaniline; they crystallise well, and volatilise with steam without decomposition. They are readily decomposed by alkalis into the hydrazine and a sulphite, and hence may be employed as a means of isolating and purifying the hydrazines. Thionylhydrazone could not be prepared from hydrazine chloride and thionylaniline, and it is probable that this compound is decomposed by water, and that free hydrazine is necessary for its preparation. Thionylparatoluidine has already been described by Michaelis and Herz (*loc. cit.*); its properties resemble those of thionylaniline. The compound *benzotoluidine sulphite*, $2NH_2{\cdot}C_7H_7,Ph{\cdot}COH,SO_2$, formed when benzaldehyde is added to a mixture of thionylparatoluidine and paratoluidine in molecular proportion in alcoholic solution, crystallises from alcohol in delicate, white needles, and melts at 119—120°.

Thionylorthotoluidine is prepared in a similar manner to the paraderivative (*loc. cit.*); it has a fainter odour than the latter, and is a bright-yellow liquid, which cannot be distilled at the ordinary pressure without decomposition; it boils at 184° under a pressure of 100 mm., does not solidify on cooling, and is easily decomposed by alkalis into orthotoluidine and a sulphite.

Thionylbenzidine, $C_{12}H_8(N{:}SO)_2$, is formed when thionyl chloride is heated for some time with benzidine dissolved in benzene; it separates on cooling in red, transparent needles, and is sparingly soluble in cold benzene, more readily in hot, and still more readily in chloroform.

Thionylparachloraniline, $C_6H_4Cl{\cdot}N{:}SO$, is prepared by dissolving parachloraniline (20 grams) in benzene (40 c.c.), and gradually adding thionyl chloride (20 grams), and heating as long as hydrogen chloride is evolved; it boils at 237°, and when cooled, solidifies forming small, faintly-yellow crystals; it melts at 36°, and is slowly decomposed by cold water, but quickly by hot water and alkalis.

Thionylmetachloraniline is a yellow liquid boiling at 233°; it solidifies when cooled.

Thionyltribromaniline, prepared by heating thionyl chloride with tribromaniline (m. p. 118°—120°) dissolved in benzene, crystallises from benzene in delicate, yellow needles, melts at 74—75°, and is easily decomposed by water.

Thionylmetanitraniline is obtained by heating thionyl chloride with metanitraniline dissolved in benzene. The crystals obtained on cooling the solution are purified by dissolving in a little benzene and precipitating with light petroleum; if the latter is carefully added, so that the two liquids only mix by degrees, large, well-formed crystals are obtained. The compound forms yellow, flat prisms, melts at 63·5°, and develops the odour of sulphurous anhydride on exposure to the air; alkalis and hot water decompose it.

Thionylparanitraniline is prepared in a manner similar to the metaderivative, which it resembles, but is more soluble in benzene; it forms delicate yellow or yellowish-red needles, and melts at 70°.

Thionylethylamine, NEt:SO, is not obtained from ethylamine hydrochloride and thionyl chloride, but is prepared as follows:—Anhydrous ethylamine (3 mols.) dissolved in several times its volume of ether is cooled in a mixture of ice and salt, and thionyl chloride (1 mol.) in ethereal solution slowly dropped in. The mixture, which is frequently shaken, is left for a long time in a closed flask; it is then filtered from ethylamine hydrochloride, and after washing the latter with ether, the ethereal solution, from which ethylamine sulphite separates if exposed to the air, is very slowly distilled on the water-bath. It is a colourless liquid of a penetrating odour, boils at 73°, and is decomposed by water with development of heat; alkalis and acids also decompose it. A. R. L.

Aromatic Sulphonic Iodides. By R. Otto and J. Tröger (*Ber.*, **24**, 478—488).—It has previously been shown by Otto that chlorine acts on metallic sulphinates with formation of the corresponding sulphonic chlorides, and the authors now find that iodine acts in a similar manner. *Paratoluenesulphonic iodide*, $C_7H_7\cdot SO_2I$, is readily obtained by adding an alcoholic solution of iodine to a concentrated aqueous solution of sodium paratoluenesulphinate, and separates as a sulphur-yellow powder, which gradually darkens on exposure to the air. It becomes brown at 80°, melts at 84—85°, loses iodine above that temperature, and dissolves in light petroleum, ether, and carbon bisulphide, the solutions gradually undergoing decomposition. When heated with water, it loses iodine, and is converted into paratoluenesulphonic acid and paratoluene disulphoxide; these may be regarded as derived from the radicle $C_7H_7SO_2$ first formed, by the action of water. Alcohol converts it into ethyl paratoluenesulphonate, and small quantities of paratoluenesulphonic acid and sulphoxide, and with ammonia, it yields paratoluenesulphonamide, the iodine being simply displaced by the amido-group. Aqueous potash acts rather differently, the iodine being displaced by potassium with formation of potassium paratoluenesulphinate, and the iodine further acted on by the alkali present, and converted into potassium iodide and iodate.

The action of molecular silver on the iodide dissolved in dry, light petroleum was studied in the hope of obtaining a disulphone, according to the equation:—

$$2C_7H_7\cdot SO_2I + 2Ag = C_7H_7SO_2\cdot SO_2\cdot C_7H_7 + 2AgI.$$

Here also, however, paratoluene sulphoxide and paratoluenesulphonic acid were obtained; it is probable that the disulphone cannot exist, but at once decomposes as follows:—

$$3(C_7H_7\cdot SO_2)_2 = C_7H_7\cdot SO_2\cdot SC_7H_7 + (C_7H_7\cdot SO_2)_2O.$$

The sulphonic anhydride remains as the portion insoluble in light petroleum, and is converted by the action of alcohol into the acid.

When paratoluenesulphonic iodide is heated on an iron plate at 100°, it decomposes with incandescence and evolution of iodine; the residue contains toluenesulphonic acid, and a small quantity of a substance which crystallises from acetic acid in small needles, melts at 192—194°, and contains both iodine and sulphur.

Benzenesulphonic iodide, $C_6H_5\cdot SO_2I$, is prepared in the same manner, and forms a somewhat darker powder. It melts at 42—45°, decomposes at a considerably higher temperature, and behaves towards reagents in exactly the same manner as the paratoluene compound. The different way in which the reaction proceeds with the several reagents makes it probable that these substances exist in two tautomeric modifications, as represented by the formulæ $R\cdot S^{vi}O_2\cdot I$ and $R\cdot S^{iv}O\cdot OI$.

An unsuccessful attempt was also made to prepare the corresponding *ethylsulphonic iodide*, but the product consisted of free ethylsulphinic acid, ethylsulphonic acid, and a little mercaptan.

H. G. C.

Action of Zinc Ethyl on Aromatic Sulphonic Iodides. By R. OTTO and J. TRÖGER (*Ber.*, **24**, 488—491).—This investigation was undertaken in the hope that the product would either be an ethyl sulphone derivative or the ethyl salt of the sulphinic acid, and thus throw some light on the question of the formulæ of the iodides, which, as suggested in the previous abstract, may possibly exist in two tautomeric forms. This anticipation has not been realised, as the product of the action is simply ethyl iodide and the zinc salt of the sulphinic acid; a similar result was obtained by Kalle (*Annalen*, **119**, 153), by treating benzenesulphonic chloride with zinc ethyl.

The reaction was carried out in light petroleum solution, and takes place almost immediately, but the zinc salt remains dissolved for some time, and only separates on allowing it to remain, or on pouring the solution into a vessel containing air or carbonic anhydride; it is then quite insoluble in light petroleum. Possibly this zinc salt exists in two tautomeric forms, corresponding with those previously given for the iodide.

H. G. C.

Aromatic Thiosulphonic Acids. By R. OTTO and J. TRÖGER (*Ber.*, **24**, 491—495).—Molecular silver acts on an aqueous solution of potassium benzenethiosulphonate with formation of silver sulphide, and the solution, after the separation of the latter, contains only potassium benzenesulphinate. Silver also converts sodium thiosulphate into sodium sulphite under the same conditions. A double potassium and silver benzenethiosulphonate may be prepared by dissolving silver chloride in a solution of potassium benzenethiosulphonate; it has the composition $C_6H_5S_2O_2K,C_6H_5S_2O_2Ag$, and crystallises in needles. Paratoluenethiosulphonic acid yields a similar double salt, also crystallising in needles.

When ferric chloride is added to a solution of potassium benzenethiosulphonate, and the mixture gently warmed, the ferric salt is obtained as an orange or reddish-yellow precipitate. If the thiosulphonate is poured into a hot solution of ferric chloride, sulphur, ferrous chloride, potassium chloride, and benzenesulphonic chloride are formed in addition. The paratoluene compound behaves in a similar manner. If potassium benzenethiosulphonate is heated with concentrated aqueous potash, one sulphur atom is eliminated in the form of sulphide, and possibly also as thiosulphate, the solution becoming yellow, and containing in addition only potassium sulphinate.

Potassium paratoluenethiosulphonate separates from water in lustrous, colourless, transparent crystals, belonging to the monosymmetric system ($a : b : c = 0{\cdot}8854 : 1 : 1{\cdot}5436$, $\beta = 60^\circ{\cdot}8'$).

H. G. C.

Behaviour of Sulphonic Chlorides towards Thiophenols and Thioalcohols in presence of Alkalis. By R. OTTO (*Ber.*, **24**, 713—716).—The ease with which the hydrogen atom of the hydroxyl group in phenols is displaced by the group $C_6H_5{\cdot}SO_2$ in aqueous alkaline solution, led the author to attempt to displace the corresponding hydrogen atom of the thiophenols by a similar group. The results obtained, however, show that the reaction takes place in a different manner, a bisulphide and a sulphinic acid being formed. Thus benzenesulphonic chloride and thiophenyl yielded phenyl bisulphide and benzenesulphinic acid in almost quantitative proportions; this is probably the best method of preparing benzenesulphinic acid. A corresponding result was obtained with benzenesulphonic chloride and thioparacresol, paratoluenesulphonic chloride and thioparacresol, and also with ethylsulphonic chloride and ethyl mercaptan.

H. G. C.

Benzaldehydesulphonic Acid. By E. KAFKA (*Ber.*, **24**, 791—797).—Benzaldehydesulphonic acid is obtained as described by Wallach and Wüsten (*Ber.*, **16**, 150). The sodium salt crystallises from water or dilute alcohol in white aggregates.

Sodium benzaldoximesulphonate, $SO_3Na{\cdot}C_6H_4{\cdot}CH{:}NOH$, is obtained by heating a faintly alkaline mixture of sodium benzaldehydesulphonate (1 mol.), hydroxylamine hydrochloride ($1\frac{1}{2}$ mols.), and sodium carbonate for one hour on the water-bath. It crystallises in white, lustrous plates, and is very easily soluble in water, less soluble in alcohol.

Sodium phenylhydrazinebenzylidenesulphonate,

$$SO_3Na{\cdot}C_6H_4{\cdot}CH{:}N_2HPh,$$

is obtained as a yellow, flocculent precipitate when the calculated quantity of phenylhydrazine, dissolved in dilute acetic acid, is added to an aqueous solution of the sodium sulphonate. It forms beautiful colourless needles, and is sparingly soluble in cold water, easily soluble in hot water, alcohol, and glacial acetic acid.

Sodium diphenylhydrazonebenzylidenesulphonate,

$$SO_3Na{\cdot}C_6H_4{\cdot}CH{:}N_2Ph_2,$$

is obtained by adding an aqueous solution of diphenylhydrazone hydrochloride to an aqueous solution of the sodium sulphonate containing the required quantity of sodium acetate. The mixture is heated on the water-bath for some time, and, on cooling, nacreous plates separate. It is sparingly soluble in cold water and alcohol, easily soluble in hot water.

Sodium α-naphthylaminebenzylidenesulphonate,

$$SO_3Na{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_{10}H_7,$$

is prepared by heating a mixture of α-naphthylamine dissolved in alcohol and an aqueous solution of the sodium sulphonate. It crystallises in beautiful, pale-yellow prisms, and is easily soluble in water, sparingly so in alcohol.

Sodium benzylidenesulphonaphthionate,

$$SO_3Na{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_{10}H_6{\cdot}SO_3Na,$$

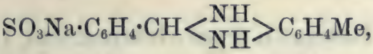
is obtained by heating sodium naphthionate with sodium benzaldehydesulphonate in aqueous solution; it crystallises in small, white needles, and is somewhat easily soluble in water, but only sparingly in alcohol.

Sodium paraphenylenediaminedibenzylidenesulphonate,

$$C_6H_4(N{:}CH{\cdot}C_6H_4{\cdot}SO_3Na)_2,$$

is obtained by heating an alcoholic solution of paraphenylenediamine with an aqueous solution of the sodium sulphonate on the water-bath. It crystallises from dilute alcohol in yellow needles, and is easily soluble in water, but only sparingly in alcohol.

Sodium metaparatoluylenediaminebenzylidenesulphonate,



$$SO_3Na{\cdot}C_6H_4{\cdot}CH{<}{\genfrac{}{}{0pt}{}{NH}{NH}}{>}C_6H_4Me,$$

is obtained by heating a mixture of orthotoluylenediamine hydrochloride and the sodium sulphonate with sodium acetate on the water-bath for 1½ hours. It is sparingly soluble in water and dilute alcohol, insoluble in absolute alcohol, and easily soluble in dilute hydrochloric acid.

Benziledisulphonic acid, $C_2O_2(C_6H_4{\cdot}SO_3H)_2$, is prepared as follows:—Barium benzaldehydesulphonate (30 parts) dissolved in alcohol (150 parts, 50—55 per cent.) and potassium cyanide (5 parts) are heated in a reflux apparatus for four hours. The product is filtered, evaporated to dryness, extracted with 85 per cent. alcohol, and the residue, which consists of benzoïndisulphonic acid, dissolved in water and precipitated with alcohol. The benzoïndisulphonic acid, which is not at all well characterised, is oxidised with strong nitric acid, and easily yields benziledisulphonic acid. The latter is separated by means of its *barium* salt, which forms a colourless, crystalline powder, extremely soluble in water, and sparingly soluble in alcohol. Benziledisulphonic acid forms with phenylhydrazine a very soluble yellow dye, which gives an intense orange-yellow colour to wool, and is fast to alkalis and acids.

Barium di-α-naphtholbenzylidenesulphonate,

$$[CH(C_{10}H_6{\cdot}OH)_2{\cdot}C_6H_4{\cdot}SO_3]_2Ba,$$

is prepared by mixing the barium salt of the sulphonic acid (10 parts) with α-naphthol (11 parts), dissolving the mixture in glacial acetic acid (60—70 parts), and gradually adding a 25 per cent. solution of hydrochloric acid (8—9 parts). The mixture is heated for seven hours on the water-bath, and must be kept from contact with water vapour; it is then filtered from barium chloride, the unattacked α-naphthylamine and acetic acid got rid of, the remaining barium precipitated with sulphuric acid, and the solution decolorised with animal charcoal. The barium salt is prepared by adding barium carbonate to the solution, is easily soluble in water and alkalis, not so soluble in dilute alcohol, and insoluble in absolute alcohol. With diazo-compounds, it yields dyes; with diazobenzenesulphonic acid, a yellowish-red; with diazotised benzidinesulphonic acid, a brownish-red, of only weak tinctorial power; with diazo-β-naphthalenesulphonic acid, a dark-red, of strong tinctorial power.

Sulphocinnamic acid, $SO_3H{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COOH$, is obtained by heating a mixture of barium benzaldehydesulphonate (6 parts), anhydrous sodium acetate (3 parts), and acetic anhydride (10 parts) in a reflux apparatus for 8—9 hours. The acid is purified by conversion into the barium salt; the latter crystallises in white aggregates, and is easily soluble in water, sparingly soluble in alcohol.

Benzaldehydesulphonic acid, when treated with nitric acid, does not yield a nitro-compound. Ammonia has no effect on it. When the barium salt is exposed to the air, or when air is led through its solution at 90—95°, no oxidation takes place. When oxidised with nitric acid, it yields metasulphobenzoic acid. E. C. R.

Extraction of Indigotin from Commercial Indigo. By T. M. MORGAN (*Chem. Centr.*, 1891, i, 76; from *J. Amer. Chem. Soc.*, **12**, 302).—The finely-powdered indigo is mixed with about an equal weight of zinc-dust, and is spread in layers of about 1 inch in thickness in a chamber through which steam can be passed; the chamber is also provided with an opening for the admission of sulphurous anhydride. The indigo is covered so as to prevent any condensed water from dropping on to it. After expelling the air, steam is allowed to pass slowly through the chamber, and the sulphurous anhydride is admitted in small quantities at a time until the reduction is complete; this occupies from one to two hours. The mass has then a dirty-yellowish or greenish-yellow appearance, and when dry does not oxidise very readily, and may be kept for several days. The indigo-white may be extracted with wood-spirit, from which pure indigotin may be obtained in crystals by exposing the solution to the air.

J. W. L.

Synthesis of Dimethylindigo from Parachloracetotoluidide and Paratolylglycin. By H. ECKENROTH (*Ber.*, **24**, 693).—When 1 part of parachloracetotoluidide or of paratolylglycin is fused with 2 parts of potash in the manner described by Flimm (Abstr., 1890, 383) or Heumann (this vol., p. 75), an orange-coloured melt is obtained, which is readily soluble in water, and on exposure to the air, deposits dimethylindigo. The latter is physically indistinguishable from ordinary indigo. H. G. C.

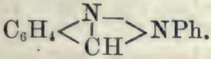
Oxidation of Hydrated Pyridine Bases: Conversion of Tetrahydroquinoline into Isatin. By C. SCHOTTEN (*Ber.*, **24**, 772—775).—Tetrahydroquinoline was prepared by reducing quinoline with tin and hydrochloric acid, the mixture steam-distilled, and the aqueous distillate shaken up with soda and benzoic chloride; benzoyltetrahydroquinoline soon separates.

Benzoylisatinic acid, $C_7H_5O{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}COOH$ (benzoylorthoamidobenzoylformic acid), is obtained by heating benzoyltetrahydroquinoline with potassium permanganate (2·5 parts) and water (20 parts); the excess of permanganate is then destroyed, the solution filtered, and the acid precipitated with hydrochloric acid. The yield amounts to 50 per cent. of the tetrahydroquinoline employed; the product in the mother liquors was not examined; carbonic anhydride and oxalic acid are formed in small quantities. Benzoylisatinic acid crystallises from solutions of its salts on acidification in colourless prisms, from dilute alcohol in very pale-yellow prisms, is quite insoluble in water, easily soluble in alcohol, not so soluble in absolute ether, and melts at 188° with formation of its anhydride. The *alkali* salts are easily soluble in water. The *barium* salt is sparingly soluble in both hot and cold water. Benzoylisatinic acid, prepared by dissolving isatin in hot dilute soda, and shaking the cold solution with benzoic chloride, was identical in every respect with the above.

Benzoylisatin is obtained from the above acid by heating it for a few minutes above its melting point, or by heating for some time with excess of acetic anhydride. It crystallises from glacial acetic acid in intensely yellow needles, which yield a yellow powder when ground up, is sparingly soluble in cold, more soluble in hot acetic acid, very sparingly soluble in alcohol and ether, and melts at 206° with a brown coloration. It is insoluble in cold dilute alkali hydroxides and carbonates, but dissolves if allowed to remain some time in contact with them in the cold, or more quickly on warming, and is converted into benzoylisatinic acid. With sulphuric acid and benzene containing thiophen, it gives as beautiful a blue as isatin itself.

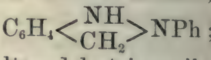
E. C. R

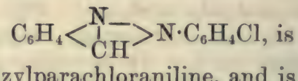
New Synthesis of Indazole Derivatives. By C. Paal (*Ber.*, **24**, 959—966).—In their investigations on dihydroquinazolines (Abstr., 1890, 1443). Paal and Krecke obtained a base having the empirical formula $C_{13}H_{10}N_2$, by the reduction of orthonitrobenzylaniline, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHBr$, with tin and hydrochloric acid. Further investigation has shown that the base is 2′-*phenylindazole*,

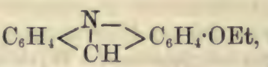
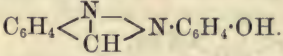


$$C_6H_4 < \begin{matrix} N- \\ | \\ CH \end{matrix} > NPh.$$

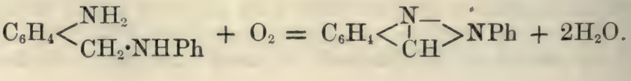
It is best prepared from the product of reduction by allowing the stannochloride to crystallise out, digesting it with ammonium sulphide, and extracting the washed residue with hot alcohol. On carefully adding water to the solution, 2′-phenylindazole separates in crystals; it melts at 83—84°, boils without decomposition at 344—345° (uncorr.), and has a molecular weight, as determined by Raoult's method, in benzene solution, agreeing with the above formula. It is not altered by nitrous acid or acetic anhydride, and may be distilled over faintly red-hot zinc-dust almost without decomposition. Further, on heating with methyl iodide and methyl alcohol, it yields a *methiodide*, $C_{13}H_{10}N_2,MeI$, which crystallises from methyl alcohol in spherical aggregates of slender, white needles, and melts at 188°. From these results, it follows that both nitrogen atoms in the compound are in the tertiary condition, and from this fact and the method by which it is obtained, it must have the constitutional formula given above. Especially noteworthy is the ease with which the indazole ring is formed, both in this and in the previous syntheses (Abstr., 1884, 440; 1885, 540; this vol., p. 312).

When 2′-phenylindazole is treated with sodium in absolute alcohol, it is converted into 2′-*phenyl*-1′ : 3′-*dihydrindazole*,  $C_6H_4<\substack{NH \\ CH_2}>NPh$; some of the indazole, however, always remains unaltered, but is easily separated by its greater solubility in alcohol. The dihydro-compound crystallises from the latter solvent in nacreous plates, melts at about 98°, forms an unstable hydrochloride, which is decomposed by water, and is oxidised to 2′-phenylindazole by ferric chloride.

2′-*Parachlorophenylindazole*,  $C_6H_4<\substack{N- \\ | \\ CH}>N\cdot C_6H_4Cl$, is obtained by the reduction of orthonitrobenzylparachloraniline, and is isolated in a similar manner to the phenyl derivative. It forms lustrous plates, readily soluble in hot alcohol, benzene, and acetic acid, sparingly in light petroleum, and melts at 138°. 2′-*Parabromophenylindazole* is obtained by the same method from orthonitrobenzylparabromaniline. It does not, however, form a stannochloride, and is obtained directly from the reduced solution in flat, colourless needles melting at 147°, and sparingly soluble in alcohol, readily in benzene and acetic acid.

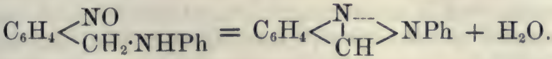
2′-*Paraphenetylindazole*,  $C_6H_4<\substack{N- \\ | \\ CH}>C_6H_4\cdot OEt$, is prepared by the reduction of orthonitrobenzylparaphenetidine. The *stannochloride* separates on cooling in yellowish plates melting at 138°. These are dissociated by hot water, with formation of free paraphenetylindazole, which crystallises from alcohol in nacreous plates, from dilute acetic acid in flat needles, and from a mixture of benzene and light petroleum in short, colourless prisms. It melts at 118°, and forms salts which are dissociated by water. On treatment with phosphorus and hydriodic acid, it is converted into ethyl iodide and 2′-*parahydroxyphenylindazole*,  $C_6H_4<\substack{N- \\ | \\ CH}>N\cdot C_6H_4\cdot OH$. The *hydriodide* of the new base separates on cooling in large, yellowish plates, melts at 200° with blackening, and is partially dissociated by water. To prepare the free base, the hydriodide is dissolved in dilute soda, dilute acetic acid added as long as a precipitate is formed, and the latter recrystallised from dilute alcohol. It is thus obtained in fascicular aggregates of short, colourless prisms melting at 195°, readily soluble in mineral acids, alcohol, acetic acid, and in aqueous alkalis. From the latter solutions, it is precipitated by carbonic anhydride, but not by dilution with water.

The exact method in which the formation of the indazole ring takes place is not quite certain. The most natural supposition is that orthamidobenzylaniline is first formed and is then further oxidised—



$$C_6H_4<\substack{NH_2 \\ CH_2\cdot NHPh} + O_2 = C_6H_4<\substack{N- \\ | \\ CH}>NPh + 2H_2O.$$

The author has, however, been unable to obtain 2′-phenylindazole from orthamidobenzylaniline itself, and thinks it possible that the nitro-group may first be reduced to the nitroso-group, the nitroso-compound then undergoing condensation in the following manner:—



$$C_6H_4<\begin{matrix}NO\\CH_2\cdot NHPh\end{matrix} = C_6H_4<\begin{matrix}N\\|\\CH\end{matrix}>NPh + H_2O.$$

H. G. C.

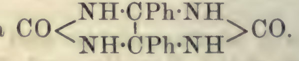
Action of Carbamide and Thiocarbamide on Dihydroxytartaric Acid, Benzile, and Benzoïn. By R. Anschütz and H. Geldermann (*Annalen*, **261**, 129—138; compare Anschütz, Abstr., 1890, 365).—Ethyl dihydroxytartrate is formed when hydrogen chloride is passed into a well-cooled alcoholic solution of sodium dihydroxytartrate; the crude product is a thick, brownish-yellow syrup, which cannot be distilled even under greatly reduced pressure. The *dihydrazone*, $C_{20}H_{22}N_4O_4$, is obtained, together with various other compounds, when crude ethyl dihydroxytartrate is treated with phenylhydrazine in alcoholic or ethereal solution; it separates from boiling alcohol in large, yellow crystals and melts at 120—121°. The *dicarbamide*, $C_{10}H_{14}N_4O_6$, is obtained as a crystalline residue when an alcoholic solution of carbamide and crude ethyl dihydroxytartrate is evaporated on the water-bath; it separates from boiling water in broad needles, melts at 245° with decomposition, and is only sparingly soluble in cold water; on hydrolysis with the theoretical quantity of sodium hydroxide, it is converted into a colourless, crystalline sodium salt of the composition $C_6H_4N_4O_6Na_2$.

Two compounds are formed when an alcoholic solution of ethyl dihydroxytartrate is evaporated with thiocarbamide; the one crystallises in long, slender needles melting above 100° with decomposition; the other forms yellow crystals and has the same percentage composition as thiohydantoïn, from which, however, it differs in appearance.

A compound of the composition $C_{16}H_{14}N_4O_2$ is obtained in crystals when benzile is heated with carbamide at 170—175° for 3 to 5 hours; it does not decompose at temperatures below 260°, is almost insoluble in alcohol, chloroform, ether, and benzene, and has possibly the constitution represented by he formula $CO<\begin{matrix}NH\cdot CPh\cdot NH\\|\\NH\cdot CPh\cdot NH\end{matrix}>CO$. When benzile and thiocarbamide are heated together at 145° in alcoholic solution, a crystalline compound of the composition $C_{16}H_{14}N_4S_2$ is obtained; this substance decomposes at 300°, and is very sparingly soluble in alcohol.

A compound of the composition $C_{15}H_{12}N_2O$, which is possibly αβ-diphenyl-μ-amidoxazole, $\begin{matrix}CPh\cdot N\\\|\\CPh\cdot O\end{matrix}>C\cdot NH_2$, is formed when benzoïn (1 mol.) is heated with carbamide at 165° in alcoholic solution for 3—4 hours (compare Hubacher, this vol., p. 222). It crystallises from hot alcohol, in which it is only moderately easily soluble, in colourless needles, and does not decompose at 260°. Thiocarbamide combines with benzoïn under the same conditions, yielding a crystalline compound which decomposes above 220°, is only sparingly soluble in alcohol, and has the composition $C_{15}H_{12}N_2S$. F. S. K.

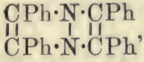
Action of Carbamide on Benzile. By A. Angeli (*Ber.*, **24**, 606).—The condensation compound of carbamide and benzile described by R. Anschütz and H. Geldermann (preceding abstract) has been previously prepared by the author (Abstr., 1890, 1290). The behaviour of tolanecarbamide (diphenylacetylenediureïne) towards acetic anhydride is best explained by the formula



$$CO<\begin{matrix}NH\cdot CPh\cdot NH\\ |\\ NH\cdot CPh\cdot NH\end{matrix}>CO.$$

J. B. T.

Action of Nascent Hydrogen on β-Benzilemonoxime. By C. U. Zanetti (*Gazzetta*, **20**, 687—692).—Polonowski (Abstr., 1888, 485) found that the product of the reduction of an alcoholic solution of β-benzilemonoxime with sodium amalgam and acetic acid is diphenylhydroxyethylamine, $OH\cdot CHPh\cdot CHPh\cdot NH_2$, melting at 161°; Braun and Meyer (1888, 700) found that a solution of β-benziloxime in soda, when treated with sodium amalgam, yields tetramethylaldine,



$$\begin{matrix}CPh\cdot N\cdot CPh\\ \|\quad\ |\ \ \|\\ CPh\cdot N\cdot CPh\end{matrix}$$

, melting at 245—246°, and Braun (Abstr., 1889, 613) obtained the base desylamine, $COPh\cdot CHPh\cdot NH_2$, by reducing it with hydrochloric acid and stannous chloride. The author finds that when a solution of β-benziloxime in absolute alcohol is treated with metallic sodium, the product consists of an impure, uncrystallisable, semi-solid mass, which may be obtained from its hydrochloride in a purer form, crystallising from dilute alcohol in white flakes melting at 158—160°, and from boiling benzene as a white powder melting at 165°. It has the same composition as diphenylhydroxyethylamine; and even after prolonged boiling with hydroxylamine hydrochloride and sodium carbonate, it nearly all crystallises out unchanged on cooling, traces only of an alkaline oil passing into solution. It is almost insoluble in water, very sparingly soluble in ether, moderately in boiling benzene, and freely in alcohol. The *hydrochloride* prepared from the pure product crystallises in long, white needles, and melts at 210° with decomposition. The *picrate* is a yellow, crystalline compound which softens and turns brown at 175°, and melts with decomposition at 178—179°. The *platinochloride*, $(C_{14}H_{15}NO)_2,H_2PtCl_6$, crystallises in brilliant, hexagonal plates which become anhydrous at 100°, soften at 180°, and melt with decomposition at 185—186°.

β-Benziloxime, when reduced in this manner, thus yields principally diphenylhydroxyethylamine and, perhaps, traces of desylamine, but no tetramethylaldine is formed. S. B. A. A.

Reduction of Acetylorthonitrobenzylparatoluidine and of Benzoylorthonitrobenzylaniline. By E. Lellmann (*Ber.*, **24**, 718).—Lellman and Stickel obtained two compounds by the reduction of acetylorthonitrobenzylparatoluidine and of benzoylorthonitrobenzylaniline, which they regarded as paratolylbenzenylethenylamidine and phenylbenzylenebenzenylamidine respectively (Abstr., 1886, 793). Söderbaum and Widman have found that these compounds are, in reality, orthamidobenzylparatoluidine and benzoylorthamidobenzylaniline (Abstr., 1890, 1258), and the author has, on re-examination of the compounds, been able to confirm this result. The first conclusion was brought about by an error in Stickel's analyses of the compounds. H. G. C.

Dyes of the Triphenylmethane Group. By E. NOELTING (*Ber.*, **24**, 553—563).—The author has shown that triamidotriphenylmethane derivatives in which a methyl group occupies an orthoposition to the fundamental carbon atom yield dyes on oxidation (*Ber.*, **22**, 2573). He now finds that the corresponding diamidotriphenylmethane derivatives also yield dyes on oxidation.

Paranitrodimethyldiamidodiphenyltolylmethane,

$$\overset{4}{N}H_2\cdot C_6H_3\overset{2}{M}e\cdot\overset{1}{C}H(C_6H_4\cdot\overset{4}{N}O_2)\cdot C_6H_4\cdot\overset{4}{N}Me_2,$$

is prepared by heating a mixture of paranitrodimethyldiamidobenzhydrol (26 grams), metatoluidine (20 grams), concentrated hydrochloric acid (40 grams), and water (40 grams) for some hours on the water-bath. The base crystallises from alcohol in yellow needles, melts at 169°, and is insoluble in water, sparingly soluble in alcohol, more soluble in benzene. The *hydrochloride* crystallises from water, in which it is easily soluble, in white leaflets. On oxidation in hot alcoholic acetic acid solution with chloranil, or in cold aqueous acetic acid with lead peroxide, it yields a beautiful, yellowish-green dye which dyes silk, wool, and cotton mordanted with tannin as easily as malachite-green, and is faster to soap than the latter. The author draws attention to the production of greens from dimethylated diamidotriphenylmethane derivatives, whilst non-methylated diamidodiphenylmethane on oxidation yields a violet dye. Paranitrodimethyldiamidotriphenylmethane also yields a green dye. The *acetyl* compound of the above leuco-base is not oxidised by lead peroxide; when treated with chloranil, however, it yields a dye which imparts an orange-red colour to cotton. The colour is similar to that from dimethylmonamidotriphenylmethane. If the acetyl group be eliminated, the colour becomes green.

Dimethyltriamidodiphenyltolylmethane is obtained from the nitro-base by reduction with tin and hydrochloric acid, or with zinc-dust and acetic acid, and crystallises from a mixture of ether and light petroleum in white needles which become violet on exposure to air. On oxidation, it yields a reddish-violet dye. The *diacetyl* compound is obtained by boiling with acetic anhydride; it crystallises from alcohol in white needles, melts at 130°, and yields a dye which imparts a violet-red colour to cotton mordanted with tannin; on eliminating the acetyl groups, the colour is changed to violet.

Paranitrotetramethyldiamidodiphenyltolylmethane is obtained by heating a mixture of nitrodimethylamidobenzhydrol (6 grams), dimethylmetatoluidine (15 grams), hydrochloric acid (10 grams), and water (20 grams) for 10 hours on the water-bath. It crystallises from ether in beautiful, yellow leaflets, melts at 193°, is easily soluble in alcohol and benzene, and on oxidation gives a beautiful yellowish-green. The *amido*-base, obtained from the nitro-base by reduction, yields a violet dye which rivals methyl-violet in shade.

Paranitrodimethyldiethyldiamidodiphenyltolylmethane, obtained in a similar way to the tetramethyl derivative, crystallises from alcohol in beautiful, yellow needles, and melts at 165—166°. Both the nitro-base and the amido-base, obtained from it on reduction, easily yield dyes on oxidation; the former giving a green, the latter a violet dye.

In the succeeding part of the paper, the author shows that diamido- and triamido-triphenylmethane derivatives, in which two methyl groups are in the ortho-position to the fundamental carbon atom, easily yield dyes on oxidation.

Tetramethyldiamidophenylditolylmethane, prepared from benzaldehyde and dimethylmetatoluidine according to the method described by Riedel, crystallises well from light petroleum and alcohol, melts at 123°, and yields a dye which colours cotton an intense green.

Paranitrotetramethyldiamidophenylditolylmethane is best prepared by heating a mixture of paranitrobenzaldehyde (12 grams), absolute alcohol (25 grams), dimethylmetatoluidine (25 grams), and concentrated sulphuric acid (15 grams) for 20 hours on the water-bath. It crystallises from a mixture of alcohol and benzene in yellow needles, melts at 224°, is sparingly soluble in alcohol, and yields a green dye resembling malachite-green.

Tetramethyltriamidophenylditolylmethane is obtained as described by Kock (Abstr., 1887, 836), and melts at 140°. On oxidation with lead peroxide and acetic acid, a dye is obtained which colours cotton, silk, and wool an intense violet: when oxidised with chloranil in dilute solution, no dye is formed, but in concentrated alcoholic acetic acid the above violet dye is obtained. The *acetyl* compound gives a green dye which, on elimination of the acetyl group, changes to violet.

Paranitrotetrethyldiamidophenylditolylmethane, prepared in a similar way to the tetramethyl compound, crystallises from alcohol in yellow needles, melts at 155°, and yields a green dye. The amido-compound yields a violet dye.

Metanitrotetramethyldiamidophenylditolylmethane, prepared in a similar way to the para-compound, crystallises in small yellow needles, melts at 170°, is easily soluble in alcohol, ether, and benzene, and yields a green dye possessing remarkable fastness to soap. The *triamido*-compound, obtained by reduction of the above, crystallises in white needles, melts at 131°, and also yields a green dye.

Orthonitrotetramethyldiamidophenylditolylmethane, prepared in a similar way to the para-compound, crystallises from a mixture of benzene and light petroleum in yellow needles, melts at 146°, and yields a bluish-green dye. The *triamido*-compound is very unstable, and could not be oxidised. The *acetyl* compound, obtained from the hydrochloride of the triamido-base, yields on oxidation a green dye.

Hexamethyltriamidophenylditolylmethane, obtained in a similar way to the above compounds, is very soluble in all solvents, and is best purified by converting it into the *picrate*, which is obtained in beautiful, yellow needles on adding picric acid to a solution of the base in hot alcohol. The base, on oxidation, yields a beautiful violet which is of a bluer shade than crystal-violet.

Hexamethyltriamidotritolylmethane is prepared by heating a mixture of ethyl orthoformate (4 grams), dimethylmetatoluidine (12 grams), and zinc chloride (10 grams) for some hours on the water-bath. It crystallises from alcohol in small, white needles and melts at 190—191°. The salts of the base are easily soluble. On oxidation, it yields a beautiful, blue dye which dyes silk, wool, and cotton mordanted with tannin very well, and rivals crystal-violet in richness. The same dye is obtained by heating dimethylmetatoluidine and aluminium chloride with a solution of carbon oxychloride in toluene.

Hexamethyltriamidotrixylylmethane, $\overset{1}{C}H(C_6H_2\overset{2.6}{Me_2}\cdot\overset{4}{N}Me_2)_3$, prepared in a similar way to the preceding compound, crystallises from alcohol in long, white needles, melts at 134—135°, and yields a green dye.

Hence the introduction of three methyl groups in the meta-position changes the violet colour of hexamethylrosaniline into blue, and of six methyl groups into green. E. C. R.

Naphthylglycollic Acid and β-Naphthyl Methyl Ketone. By R. Schweitzer (*Ber.*, **24**, 546—549).—Both α-naphthyl methyl ketone and β-naphthyl methyl ketone are formed by the action of acetic chloride on naphthalene dissolved in carbon bisulphide in the presence of aluminium chloride. The β-compound is filtered from the α-compound and recrystallised from light petroleum. It melts at 54° and boils at 306° (Claus and Fersteegen give 51·5—52° and 301—303°). The α-compound cannot be obtained in a pure condition from the mother liquors.

β-Naphthyl methyl ketone dibromide, $C_{10}H_7\cdot CO\cdot CHBr_2$, is obtained by the action of bromine on β-naphthyl methyl ketone dissolved in carbon bisulphide, and melts at 101°.

β-Naphthylglycollic acid, $C_{10}H_7\cdot CH(OH)\cdot COOH$, is obtained by allowing the above dibromide to remain in contact with aqueous potash (1 : 10) in the cold for 8—14 days. It melts at 158° (Claus and Fersteegen, 176°), is sparingly soluble in light petroleum and ether, more soluble in hot water, and easily soluble in acetic acid and hot alcohol. By oxidation with potassium permanganate, β-naphthaldehyde and β-naphthoic acid are formed. On sublimation, no pure product could be obtained. The *silver* salt is insoluble in cold or hot water. The *calcium* and *magnesium* salts are sparingly soluble. The *ethyl* salt crystallises from light petroleum in tufts of needles, and melts at 87°. The *methyl* salt crystallises from alcohol in needles and melts at 75°. The acid is more readily obtained by brominating the mixed ketones, treating with potash, and converting into barium salts. On crystallising the barium salts from a large quantity of hot water, only the β-salt separates on cooling; and by decomposing this the acid is obtained quite pure.

β-Acetylnaphthylglycollic acid is formed by dissolving naphthylglycollic acid in acetic anhydride and crystallising the product from dilute acetic acid. It melts at 150° (uncorr.).

β-Naphthylglycolamide separates from an ammoniacal alcoholic solution of the ethyl salt when it is allowed to remain for 8—14 days. It crystallises from absolute alcohol in plates and melts at 227—228°.

β-Naphthylacetic acid, $C_{10}H_7·CH_2·COOH$, is obtained by reducing naphthylglycollic acid with hydrogen iodide; it crystallises from water in plates and melts at 141°. The *methyl* and *ethyl* salts form needles which melt at the temperature of the hand, and have an odour resembling that of acetic acid. The *barium* salt crystallises from water in plates.

α-Naphthylglycollic acid is obtained from the mother liquors of the barium salt of the β-compound when the latter is prepared from the mixed ketones. The acid so obtained is converted into the *methyl* salt and this is extracted by shaking with petroleum, when only the α-compound dissolves. The latter crystallises in microscopic needles and melts at 79° (uncorr.). The ethereal salt is treated with alcoholic caustic soda and the resulting sodium salt decomposed with hydrochloric acid and the acid recrystallised from water. It melts at 91—93° (uncorr.), and on oxidation with dilute nitric acid yields α-naphthaldehyde. The *barium* salt is easily soluble in water. The *ethyl* salt is an oil. E. C. R.

β-Isoamylnaphthalene. By G. ODDO and E. BARABINI (*Gazzetta*, **20**, 719—720).—The isoamylnaphthalene obtained by Roux (Abstr., 1884, 1357) by the action of aluminium chloride on naphthalene and amyl bromide, has now been prepared by the authors from β-bromonaphthalene by treating it with sodium and isoamyl bromide according to Fittig and Tollens' method. The product boils between 289—292°, has the composition $C_{15}H_{18}$, and forms a *picrate* extremely soluble in alcohol, which crystallises in slender needles and melts at 108—110°. S. B. A. A.

Derivatives of Chrysene. By R. ABEGG (*Ber.*, **24**, 949—958).—The amidochrysene previously described by the author (Abstr., 1890, 789) is identical with the compound obtained by Bamberger and Burgdorf (Abstr., 1890, 1312), the difference of 3° in the melting point being probably due to variations in the thermometers employed. Amidochrysene may be readily converted into other derivatives containing the radicle $C_{18}H_{11}$, for which the author proposes the term *chrysyl.*

Benzoylamidochrysene, $C_{18}H_{11}·NHBz$, is obtained by the action of benzoic chloride and aqueous soda on amidochrysene; it is a yellowish-brown substance, melts at 248°, and is moderately soluble in cold benzene and toluene, readily in the hot liquids and in cumene. *Ethyl chrysylcarbamate*, $C_{18}H_{11}·NH·COOEt$, is obtained in a similar manner by the action of ethyl chloroformate on amidochrysene, and is a white, crystalline compound melting at 214°. By the action of carbonyl chloride on amidochrysene in toluene solution, a substance is obtained which is insoluble in all ordinary solvents and could not be prepared in a pure condition; it is probably *dichrysylcarbamide* or *chrysylcarbimide.*

Acetamidochrysene or *chrysylacetamide*, $C_{18}H_{11}·NHAc$, is prepared by heating amidochrysene with acetic acid and some acetic anhydride; it crystallises from acetic acid or amyl alcohol in slender, greenish needles and melts at 285°. If acetic anhydride be employed alone, *diacetamidochrysene*, $C_{18}H_{11}NAc_2$, is obtained; it closely resembles the monacetyl compound, but melts at 206—208°. The comparative facility with which both hydrogen atoms of the amido-group are substituted by acetyl is very remarkable.*

By the action of bromine-water on chrysylacetamide, it yields *bromochrysylacetamide*, $C_{18}H_{10}Br{\cdot}NHAc$; the latter separates from acetic acid in brown, seemingly amorphous flakes, which ball together at 180° without melting, and decompose at 215°. Fuming nitric acid dissolves chrysylacetamide, with formation of *dinitrochrysylacetamide*, $C_{18}H_9(NO_2)_2{\cdot}NHAc$; the latter separates from light petroleum in amorphous plates, melts at 160°, and on heating with concentrated hydrochloric acid at 120° is converted into a glassy mass consisting of *dinitrochrysylamine hydrochloride*, $C_{18}H_9(NO_2)_2{\cdot}NH_2,HCl$.

When chrysylacetamide or chrysyldiacetamide is heated with nitric acid of sp. gr. 1·25, nitrous fumes are evolved, and the nitrochrysoquinone, $C_{18}H_9O_2NO_2$, described by Bamberger and Burgdorf, formed (*loc. cit.*). It melts at 252°, and on treatment with hydriodic acid and phosphorus, yields *amidochrysoquinol hydriodide*, $C_{18}H_9(OH)_2{\cdot}NH_2,HI$, which readily passes into the corresponding *amidochrysoquinone* salt, $C_{18}H_9O_2{\cdot}NH_2,HI$, mixed with some periodide. If chrysoquinone hydriodide is boiled with silver chloride and platinum chloride added, the *platinochloride*, $(C_{18}H_9O_2{\cdot}NH_2)_2,H_2PtCl_6$, is formed. When nitrochrysoquinone is reduced with tin and hydrochloric acid, amidochrysoquinone is first formed, and is afterwards converted into amidochrysoquinol hydrochloride.

Chrysylthiocarbimide, $C_{18}H_{11}{\cdot}N{\vdots}CS$.—When amidochrysene is boiled with carbon bisulphide, it is simply dissolved, but if potash and sufficient alcohol for its solution be added, a greenish product remains on evaporating off the carbon bisulphide, from which hot water extracts potassium xanthate and sulphide; from the residue, acetic acid extracts chrysylthiocarbimide. It crystallises in pale-green or brownish needles, melts at 176°, is readily soluble in acetic acid and carbon bisulphide, scarcely in alcohol, ether, and light petroleum. The residue insoluble in acetic acid is a greenish powder melting at 225°, and only soluble in hot benzene; it appears to be impure *dichrysylthiocarbamide*, $CS(NHC_{18}H_{11})_2$. *Monochrysylthiocarbamide*, $C_{18}H_{11}{\cdot}NH{\cdot}CS{\cdot}NH_2$, is prepared by the action of ammonia on a benzene solution of chrysylthiocarbimide; it forms almost white crystals and melts at 238° with decomposition. The crystals contain 1 mol. benzene of crystallisation, which is not evolved at 100°. From a toluene solution, crystals are obtained also melting at 238°, but free from toluene, and if phenylcarbamide be prepared in benzene solution, it is also free from benzene. *Methylchrysylthiocarbamide*, $C_{18}H_{11}{\cdot}NH{\cdot}CS{\cdot}NHMe$, formed by the action of methylamine on a benzene solution of chrysylthiocarbimide, melts at 231°, and also contains no benzene of crystallisation. *Phenylchrysylthiocarbamide*, $C_{18}H_{11}{\cdot}NH{\cdot}CS{\cdot}NHPh$, is prepared by treating a benzene solution of amidochrysene or chrysylthiocarbamide with the calculated quantity of phenylthiocarbimide or aniline respectively, and separates after 1—3 days in yellowish-white crystals melting at 186°. It is, however, only formed from solutions of chrysyl derivatives; if chrysylamine and phenylthiocarbamide are heated together alone, chrysylthiocarbimide and aniline are formed, the latter at once combining with part of the phenylcarbimide, with formation of diphenylcarbamide. H. G. C.

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* *Note by Abstractor.*—Amidoacenaphthene behaves in a similar manner when heated with acetic anhydride (*Ber.*, **21**, 1458).

Formation of an Asphalt-like Substance from Oil of Cassia. By E. HIRSCHSOHN (*Chem. Centr.*, 1891, i, 87—88; from *Pharm. Zeit. Russ.*, **29**, 692—695).—When oil of cassia was heated for four hours at 260—280°, it became dark-coloured and lost 12 per cent. of its weight; when the heating was continued up to 355° during six hours, a further loss of 7 per cent. was experienced, and the distillate amounted to 16 per cent. The flask, covered with glass wool and asbestos, was now heated for six hours, when 15 per cent. more distillate was obtained, and it was finally heated for six hours longer. The residue remaining amounted in one case to 54 per cent., and in a second to 60 per cent. of the original oil. The distillates contained a substance similar to xylene, acetic acid, and phenol. The residue in the retort was a black solid, and could be readily reduced to a strongly electrical powder; it smelt like asphalt and behaved with solvents similarly to Trinidad asphalt or artificial asphalt. The author suggests that these observations on oil of cassia explain to some extent the formation of asphalt in nature, possibly brought about by superheating resins and ethereal oils under pressure.

J. W. L.

Pyridine Compounds. By R. VARET (*Compt. rend.*, **112**, 390—392).—When finely divided and dry cadmium bromide is added to pyridine, heat is developed and a white paste is formed. Excess of pyridine is then added and the mixture is heated on a water-bath for two hours, and allowed to cool with occasional agitation. After some time, the amorphous precipitate changes into a crystalline precipitate, which is rapidly dried between filter paper. The product consists of small, brilliant, white crystals of the composition $CdBr_2,6C_5NH_5$. It is only slightly soluble in pyridine; boiling water converts it into a curdy precipitate which completely dissolves, and on cooling, long needles of a different compound of cadmium bromide and pyridine separate. The compound $CdBr_2,6C_5NH_5$ loses all its pyridine when heated.

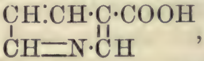
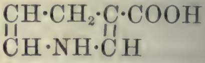
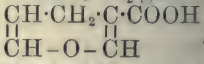
Silver cyanide under similar conditions yields transparent, acicular prisms of the compound $AgCy,C_5NH_5$, slightly soluble in pyridine and decomposed by water. When exposed to air, the crystals become opaque, and then brown, and at 110° they lose the whole of their pyridine.

Mercuric cyanide yields granular, transparent crystals of the compound $HgCy_2,2C_5NH_5$, very soluble in pyridine, especially on heating. They lose their pyridine at 110°.

Cuprous cyanide yields large, yellow lamellæ of the composition $Cu_2Cy_2,4C_5NH_5$, very soluble in warm pyridine. When exposed to the air, it evolves pyridine and it loses the whole of this substance at a temperature below that at which cuprous cyanide decomposes.

Cuprous iodide yields small, yellow crystals of the compound $Cu_2I_2,2C_5NH_5$, very soluble in hot pyridine, less soluble in the cold. When treated with 10 vols. of ether, it becomes white, but does not lose all its pyridine even after several days. When exposed to air, it becomes green, then brown, and when heated, it loses the whole of its pyridine. C. H. B.

Non-nitrogenous Acids derived from Pyridinecarboxylic Acids. By H. WEIDEL (*Monatsh.*, **11**, 501—525).—The author has previously (*Sitzber. k. k. Akad. Wien*, 1874, 239; 1879, 460) investigated the action of sodium amalgam on cinchomeronic acid, whereby ammonia and cinchonic acid, $C_7H_8O_6$, are obtained. When distilled, the last-named compound loses water and carbonic anhydride, forming the anhydride of dimethylfumaric acid (pyrocinchonic anhydride), a substance which takes up water and hydrogen to form an acid isomeric with adipic acid, and melting at 182°. In order to determine the constitution of cinchonic acid and other non-nitrogenous acids formed under similar conditions, the author has fully studied the products derived from the three pyridinecarboxylic acids by the action of sodium amalgam, and finds that these acids are almost quantitatively converted into saturated bibasic hydroxy-acids, according to the equation $C_6H_5NO_2 + H_2 + 3H_2O = C_6H_{10}O_5 + NH_3$. The three hydroxy-acids are derived from three isomeric adipic acids, and, since they have the hydroxyl group in the δ-position relatively to one of the carboxyl groups, are partially, with loss of water, converted into lactonic acids. The products of the action of sodium amalgam on the carboxylic acids consist, in fact, of the hydroxy-acids and the corresponding lactonic acids.

Products from Nicotinic Acid.—Nicotinic acid (40 grams) was dissolved in water (800 c.c.) containing potash (200 grams), and the resulting solution heated to the boiling point and treated with 4 per. cent. sodium amalgam, added little by little until no more ammonia was evolved, the operation lasting 3—4 hours. The product was made slightly acid with hydrochloric acid, evaporated to dryness, and exhausted with alcohol, the extract again evaporated and freed from potassium chloride and a resinous, nitrogenous substance by solution in absolute alcohol and addition of ether. The almost colourless, syrupy acid obtained on evaporation of the ethereal alcoholic solution, which crystallised only after some months, was dissolved in three times its weight of absolute alcohol, saturated with hydrogen chloride, and the product repeatedly fractionated under a reduced pressure of 60 mm., whereby two distinct fractions were obtained, one boiling at 184° (60 mm.), the other at 245—247° (56 mm.). The fraction of lower boiling point proved to be diethyl chloroglutarate, $C_4H_7Cl(COOEt)_2$, since sodium amalgam reduced it to α-methylglutaric acid, $COOH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, which melts at 75·7° (Wislicenus and Limpach, *Annalen*, **192**, 134). The fraction of higher boiling point was a colourless, syrupy liquid, having a bitter, burning taste. On analysis, it gave numbers corresponding with the formula $C_8H_{14}O_4$; when saponified with baryta-water, it furnished the salt $C_6BaH_8O_5$, and on treatment with phosphorus diiodide and water was converted into an iodo-acid, which, on reduction with zinc and sulphuric acid, also gave α-methylglutaric acid. Both the compounds $C_4H_7Cl(COOEt)_2$ and $C_8H_{14}O_4$ consequently give rise to a (γ- or δ-) hydroxy-α-methylglutaric acid, $C_6H_{10}O_5$, capable of furnishing the lactone $C_6H_8O_4$. The original non-nitrogenous products derived from nicotinic acid must, therefore, be regarded as a mixture of hydroxy-α-methylglutaric acid and the corresponding lactone, and their behaviour makes it probable that the hydroxyl group occupies the δ-position relatively to the carboxyl group. This view is confirmed by the formation of piperidone when chloro-α-methylglutaric acid is treated with potassium phthalimide, and the resulting product treated with hydrochloric acid, and by the fact that the original reduction product on dry distillation furnishes a mixture of a bibasic acid, $C_6H_8O_4 + H_2O$, melting at 133·5°, which is easily reduced to methylglutaric acid and an oil, most probably δ-valerolactone, boiling at 222—226° (56 mm.). The formation of δ-hydroxy-α-methylglutaric acid from nicotinic acid is explained by supposing that the nicotinic acid,  $\begin{array}{l} CH{:}CH{\cdot}C{\cdot}COOH \\ | \qquad\quad\; \| \\ CH{=\!=}N{\cdot}CH \end{array}$, first of all takes up two atoms of hydrogen, the linkage shifting,  $\begin{array}{l} CH{\cdot}CH_2{\cdot}C{\cdot}COOH \\ \| \qquad\quad\;\; \| \\ CH{\cdot}NH{\cdot}CH \end{array}$; the dihydro-compound then reacts with 1 mol. of water, oxygen is substituted for imidogen, and ammonia evolved,  $\begin{array}{l} CH{\cdot}CH_2{\cdot}C{\cdot}COOH \\ \| \qquad\quad\;\; \| \\ CH{-}O{-}CH \end{array}$. By the addition of another molecule of water, the closed chain is then broken, and the compound $OH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}C(COOH){:}CH{\cdot}OH$ formed, and this in its turn by assimilation, loss, and further assimilation of water, gives rise to the compounds

$$CH(OH)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH(OH)_2,$$
$$COH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH){\cdot}COH, \text{ and}$$
$$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOH){\cdot}CH_2{\cdot}OH$$

respectively.

Products from Isonicotinic Acid.—Isonicotinic acid (pyridine-γ-carboxylic acid) is more readily acted on by sodium amalgam than is nicotinic acid. On treating the product with alcohol and hydrochloric acid and distilling, two fractions were obtained; the one, boiling at 188—191° (63 mm.), has the formula $C_{10}H_{17}ClO_4$, and is converted by water at 100° into the acid originally present in the reduction product; the other, boiling at 240—244° (63 mm.), has the formula $C_8H_{12}O_4$, is converted by baryta-water into the non-crystalline barium salt, $C_6H_8BaO_5$, and gives, on treatment with phosphorus diiodide and water, a readily soluble iodoethylsuccinic acid which melts at 152°, and is reduced by zinc and sulphuric acid to Huggenberg's ethylsuccinic acid (m. p. 98·7°).

Products from Picolinic Acid.—Picolinic acid (pyridine-α-carboxylic acid) is as readily reduced as isonicotinic acid, and gives what is most probably δ-hydroxyadipic acid, $COOH{\cdot}[CH_2]_3{\cdot}CH(OH){\cdot}COOH$. On treating the syrupy reduction product with phosphorus diiodide, *adipic acid*, melting at 151° and agreeing in the crystallographic characteristics of its ammonium salt with Arppe's acid melting at 148—149° (*Annalen*, **149**, 220), was formed. G. T. M.

Piperylbiguanide. By E. BAMBERGER (*Ber.*, **24**, 605).—Dicyanodiamide combines with piperidine at the ordinary temperature to form *piperylbiguanide*, $NH_2·C(NH)·NH·C(NH)·C_5NH_{10}$; this crystallises readily, and yields a characteristic *cupro-derivative*, which is deposited in rose-coloured needles. J. B. T.

Piperidinecarboxylic Acids. By A. LADENBURG (*Ber.*, **24**, 640—643).—α-Piperidinecarboxylic acid (pipecolinic acid), $C_6H_{11}NO_2$, can be obtained by reducing picolinic acid; it is isolated in the form of the hydrochloride, $C_6H_{11}NO_2,HCl$. This salt separates from very dilute hydrochloric acid in small, nodular crystals, melts at 264°, and is soluble in alcohol. It has been previously obtained by Ost (Abstr., 1883, 791), but only in an impure condition. α-Piperidinecarboxylic acid is most easily obtained in the free state by decomposing the sulphate with the theoretical quantity of barium hydroxide; it separates from alcohol in crystals, is readily soluble in water, and forms a blue, readily soluble copper salt. The *platinochloride* forms large, monoclinic crystals, $a : b : c = 1·2880 : 1 : 1·0902$; $\beta = 66° 37'$, and melts at 184°. The *aurochloride* is readily soluble, and is decomposed when boiled with water with evolution of carbonic anhydride.

Methyl α-piperidinecarboxylate hydrochloride, $C_7H_{13}NO_2,HCl$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises from alcohol in small, colourless needles, melts at 191° with decomposition, and is readily soluble in water, but more sparingly in alcohol. The *platinochloride*, $(C_7H_{13}NO_2)_2,H_2PtCl_6$, forms well-defined prisms; the *aurochloride* is readily soluble. When a solution of the hydrochloride of the methyl salt is treated with potassium nitrite, the *nitroso*-derivative, $C_7H_{12}NO_2·NO$, is deposited as an oil.

Hexahydronicotinic acid (*nipecotinic acid*) *hydrochloride*,

$$C_6H_{11}NO_2,HCl,$$

forms small crystals and melts at 235°; the *platinochloride* crystallises well and melts at 210—212°. F. S. K.

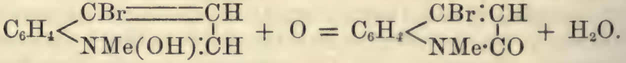
Piperazine. By A. BISCHLER (*Ber.*, **24**, 716—718).—Paradinitrosodiphenylpiperazine is acted on by alkalis in the same way as nitrosodimethylaniline, &c., piperazine and in all probability nitrosophenol being formed. To carry out the reaction, paradinitrosodiphenylpiperazine is boiled with aqueous potash and a little alcohol; it dissolves after a time, and the alcohol is then distilled off, more potash added, and the product distilled until only small quantities of liquid pass over. The alkaline distillate is treated with hydrochloric acid, and the piperazine hydrochloride purified by precipitation from its aqueous solution with absolute alcohol; it is thus obtained in snow-white, matted needles having the composition $C_4H_{10}N_2,2HCl + H_2O$. The *platinochloride*, $C_4H_{10}N_2,H_2PtCl_6$, forms yellow, four-sided plates, and the *dibenzoyl* compound crystallises in transparent, rhomboïdal crystals, and melts at 190°. H. G. C.

1-Methyl-3-diphenyl-4.5-diphenylpyrrolone. By F. KLINGEMANN (*Ber.*, **24**, 516—519).—1-Methyl-3-diphenyl-4.5-diphenylpyrrolone is obtained when the methylamide of benzoyltriphenylpropionic acid is boiled with alcoholic potash and the solution precipitated with water. It crystallises from acetic acid in beautiful, yellow crystals, and melts at 159°. These crystals contain a small quantity of the unaltered methylamide, which can be separated by recrystallisation from carbon bisulphide. The product crystallises from alcohol in small, yellow plates. It was obtained in measurable crystals from ethyl acetate, as also was the product from dibenzoylstilbene and methylamine, and that from benzoyltriphenylpropiomethylamide, by distillation (Trans., 1891, 146). These three compounds are crystallographically identical. The crystals belong to the monosymmetric system, $a : b : c = 0·79308 : 1 : 0·92709$; $\beta = 89° 41'$. A full description of the crystals is given in the paper. The author points out that the action of alcoholic potash on benzoyltriphenylpropiomethylamide is similar to the action of alkalis on methylhydrastamide.

E. C. R.

Substituted Ammonium Compounds. By H. DECKER (*Ber.*, **24**, 690—692).—The action of alkalis on the compounds of quinoline derivatives with the alkyl haloïds has been frequently examined, but the results are not concordant; the author has, therefore, repeated the experiments on a wider basis, employing the methiodides or ethiodides of 22 derivatives of quinoline, isoquinoline, and acridine. He finds that the first action of alkalis is to convert the compounds into the corresponding ammonium hydroxides, which, however, can only be isolated in certain cases, owing to further reactions taking place. Only α-nitro-γ-bromoquinolinium hydroxide and methylphenylacridinium hydroxide have been obtained in the crystalline condition.

These hydroxides readily pass into the corresponding ethoxy-compounds when gently warmed with alcohol, and also oxidise rapidly in the air or when treated with alkaline potassium ferricyanide, yielding well-crystallised substances with a strong lustre, which melt about 100° higher than the parent substances. They are formed from the ammonium hydroxide by the loss of two atoms of hydrogen, and are identical with the lactam-ethers. Thus, with γ-bromoquinoline, the reaction proceeds as follows:—

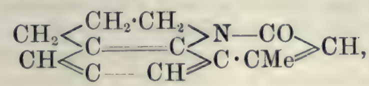


$$C_6H_4<\begin{matrix}CBr{=\!=\!=\!=}CH\\ NMe(OH){:}\overset{|}{C}H\end{matrix} + O = C_6H_4<\begin{matrix}CBr{:}CH\\ NMe{\cdot}\overset{|}{C}O\end{matrix} + H_2O.$$

Acridine also yields a new base, in which the oxygen atom probably occupies the meso-position, but phenylacridinium hydroxide is not attacked by potassium ferricyanide.

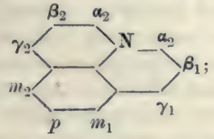
H. G. C.

Juloles. By A. REISSERT (*Ber.*, **24**, 841—856).—Ethyl acetoacetate (10 grams) is heated with tetrahydroquinoline in molecular proportion for about two hours in a reflux apparatus; a pale-red, viscid liquid is formed which contains *acetoacetic tetrahydroquinolide*, $CH_2Ac·CO·C_9NH_{10}$. On treating this compound with sulphuric acid at low temperatures and neutralising with soda, a compound is precipitated which crystallises from water or light petroleum in colourless, somewhat lustrous needles melting at 129·8° (corr.); it is readily soluble in concentrated mineral acids, and is recovered unchanged on dilution; it has the formula



$$\begin{array}{l}\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{C=\!=\!=\!=C}\end{matrix}>\mathrm{N-CO}\\ \mathrm{CH}\lessdot\begin{matrix}\\ \mathrm{C-\!-\!-CH}\end{matrix}\gtrdot\mathrm{C\cdot CMe}\end{array}>\mathrm{CH},$$

and the author proposes to term it α_1-*keto*-γ_1-*methyljuloline;* the different positions in the rings are distinguished as follows:—



the addition of 2 atoms of hydrogen to juloline gives *julolidine*, whilst the compound with 2 atoms of hydrogen less is called *julole.* The above ketomethyljuloline forms salts with acids, does not yield a phenylhydrazone, and has no physiological action. The *hydrochloride*, $C_{13}H_{13}NO,HCl + 1\frac{1}{2}H_2O$, is crystalline, and decomposes when heated at 100°. The *platinochloride* crystallises from concentrated hydrochloric acid in pale, orange-yellow needles, and blackens at about 200°. On treating the ketomethyljuloline with bromine in benzene solution, a dibromo-additive compound is formed, which is excessively unstable, and has not yet been isolated; by boiling with water, hydrogen bromide is eliminated, and β_1-*bromoketomethyljuloline* is obtained, crystallising from hydrochloric acid in colourless, voluminous needles melting at 178·5° (corr.). A *dibromo-derivative* of the formula $C_{13}H_{11}NOBr_2$ is formed by heating the juloline with 2 mols. of bromine at 100° under pressure; it is deposited from absolute alcohol in small, hard, yellow, rhombic crystals, melts at 153° (corr.), and is insoluble in hot concentrated hydrochloric acid.

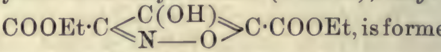
Nitrous acid appears to have no action on ketomethyljuloline, whilst nitric acid only acts in presence of concentrated sulphuric acid; two isomeric *nitro-substitution* products of the formula $C_{13}H_{12}NO{\cdot}NO_2$ are formed; the first crystallises from glacial acetic acid in pale-yellow needles, melts at 223·8° (corr.), and is sparingly soluble in alcohol. The isomeric derivative is contained in the mother liquors, crystallises from dilute alcohol in small, yellow needles, and melts at 149·1° (corr.).

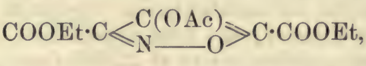
The oxidation of the ketomethyljuloline is best accomplished by dissolving it in dilute sulphuric acid, and adding 4·5 parts of potassium permanganate dissolved in hot water; as soon as the addition is completed, the solution is rapidly boiled and filtered; on cooling, *α-hydroxylepidine*-1-*carboxylic acid* is deposited; it crystallises from dilute alcohol in small, colourless needles, melts at 312·4° (corr.), and is insoluble in benzene, light petroleum, ether, and chloroform. Two other acids are also formed in small quantity during the oxidation; the one is insoluble in ammonia, crystallises from dilute acetic acid, and melts at 245°. The second acid is separated from the lepidinecarboxylic acid by treatment of the aqueous solution with ether, melts at about 230°, and is free from nitrogen.

Silver hydroxylepidinecarboxylate, $C_{11}H_8NO_3Ag$, is the most characteristic salt; it is crystalline and very sparingly soluble, and on distillation yields α-hydroxylepidine. It thus appears that the action of tetrahydroquinoline on ethyl acetoacetate is precisely analogous to that of aniline. J. B. T.

Action of Nitrous Acid on Ethyl Acetonedicarboxylate. By H. v. Pechmann (*Ber.*, **24**, 857—867).—Ethyl acetonedicarboxylate is treated with 10—15 drops of alcoholic hydrochloric acid and amyl nitrite in molecular proportion; after remaining for an hour at the ordinary temperature, the liquid is heated on the water-bath, dissolved in sodium carbonate solution, the amyl alcohol removed, and the residue, after acidifying, extracted with ether; after the removal of the ether by evaporation, a yellow, viscid, undistillable liquid is obtained consisting of *ethyl nitrosoacetonedicarboxylate*,

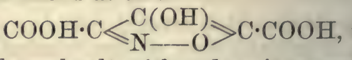
$$\mathrm{NOH{:}C(COOEt){\cdot}CO{\cdot}CH_2{\cdot}COOEt}.$$

By the action of nitrous acid on this nitroso-compound, or by treating ethyl acetonedicarboxylate with amyl nitrite (3 mols.), *ethyl hydroxyisoxazoledicarboxylate*,  $\mathrm{COOEt{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OH)}}{\mathrm{N{-}{-}O}}{>}\mathrm{C{\cdot}COOEt}$, is formed, which crystallises from dilute alcohol in long, silky, lustrous, concentric needles, and melts at 104—105°; the yield is 75 per cent. of theory. The reaction which takes place is probably represented by the equation $C_9H_{14}O_5 + 3HNO_2 = C_9H_{11}NO_6 + 3H_2O + 2NO$. In small quantities the isoxazole may be distilled without decomposition; ferric chloride gives a red coloration, alkalis and alkaline carbonates a yellow one, but on testing with phenol and sulphuric acid, the isonitroso-reaction is not observed; by the action of phosphorus pentachloride, an uncrystallisable compound is formed, from which the isoxazole is regenerated on the addition of water; sodium amalgam causes the production of substances which are difficult to isolate, and have strong reducing properties. The *acetyl derivative*,



$$\mathrm{COOEt{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OAc)}}{\mathrm{N{-}{-}O}}{>}\mathrm{C{\cdot}COOEt},$$

is obtained by the action of acetic anhydride; it crystallises from dilute alcohol in lustrous needles, and melts at 42°.

Hydroxyisoxazoledicarboxylic acid,  $\mathrm{COOH{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OH)}}{\mathrm{N{-}{-}O}}{>}\mathrm{C{\cdot}COOH}$, is prepared by the hydrolysis of the ethereal salt with soda; it crystallises from water with 2 mols. H_2O in prisms, becomes brown at about 145°, and melts at 183—184° or at 176—177°, according to whether the heating is done quickly or slowly. The *trisodium salt* is readily soluble in water, and crystallises in yellow needles; the *disodium salt* crystallises in colourless plates, and is formed by the addition of acetic acid to the trisodium derivative; the *monosodium salt*, $C_5H_2NaNO_6 + 2H_2O$, is obtained by treating the trisodium salt with hydrochloric acid, and crystallises in aggregates of small needles. The *silver salt*, $C_5HAg_2NO_6$, is crystalline.

Methoxyisoxazoledicarboxylic acid, $\mathrm{COOH{\cdot}C}\left<\begin{matrix}\mathrm{C(OMe)}\\ \mathrm{N\text{——}O}\end{matrix}\right>\mathrm{C{\cdot}COOH} + H_2O$, crystallises from a mixture of ethyl acetate and light petroleum in small, colourless needles, and melts at 157—158° with previous softening at 90—100°. The *diethyl salt* melts at 31°, and boils at 200—210° under a pressure of 40 mm. The *sodium salt*, $C_6H_4NO_6Na + 2H_2O$, is deposited from water, in which it is sparingly soluble, in long, lustrous crystals. The *silver salt*, $C_6H_3NO_6Ag_2$, explodes on heating.

Ethyl isoxazoledicarboxylate is oxidised by the action of concentrated nitric acid or of bromine, hydrogen cyanide being evolved in considerable quantity; on treating the product with phenylhydrazine, *ethyl phenylhydrazonemesoxalate*, $\mathrm{COOH{\cdot}C(N_2HPh){\cdot}COOEt}$, is formed; this crystallises from alcohol in pale-yellow needles, melts at 115°, and is soluble in alkalis; with ferric chloride, a dull yellow coloration is obtained, changing to dark-red; potassium dichromate yields a violet solution. Phenylhydrazonemesoxalic acid is prepared by the hydrolysis of the preceding compound with soda.

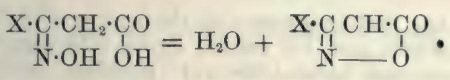
This synthesis of isoxazole derivatives corresponds with the formation of pyrazolines and pyrazoles from the phenylhydrazones of unsaturated aldehydes and ketones, since it is probable that ethyl nitrosoacetonedicarboxylate reacts in its tautomeric form

$$\mathrm{COOEt{\cdot}C(NOH){\cdot}C(OH){:}CH{\cdot}COOEt},$$

and yields the unknown isoxazoline, $\mathrm{COOEt{\cdot}C}\left<\begin{matrix}\mathrm{CH(OH)}\\ \mathrm{N\text{———}O}\end{matrix}\right>\mathrm{CHPh}$, which is oxidised, at the moment of its formation, to the isoxazole.

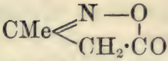
J. B. T.

Action of Hydroxylamine on β-Ketonic Acids and β-Diketones. By A. Hantzsch (*Ber.*, **24**, 495—506).—The author has already shown that the oximes of the α-ketonic acids rarely exist in both the possible stereo-isomeric forms (this vol., p. 443). With the β-ketonic acids, no case has been found in which both stereo-isomeric oximes exist, and, indeed, no oxime has been obtained in the free state, owing to the fact that, like the γ-hydroxy-acids, they readily form anhydrides:



$$\begin{matrix}\mathrm{X{\cdot}C{\cdot}CH_2{\cdot}CO}\\ \mathrm{N{\cdot}OH\quad OH}\end{matrix} = H_2O + \begin{matrix}\mathrm{X{\cdot}C\ CH{\cdot}CO}\\ \mathrm{N\text{——}O}\end{matrix}.$$

The formation of such anhydrides, which are best termed, according to Claisen's suggestion, "isoxazolones," shows that the oximes from which they are formed have the β-configuration.

The action of hydroxylamine on ethyl acetoacetate has been already examined by Westenberger (Abstr., 1884, 581), but the author has not been able to confirm all his results, some of his products having evidently been impure. By the action of hydroxylamine in alkaline solution, and subsequent acidification, the chief product is *methyl* *isoxazolone*,  $\mathrm{CMe}<\begin{matrix}\mathrm{N-O}\\ \mathrm{CH_2\cdot CO}\end{matrix}$, the formation of which corresponds with that of methylphenylpyrazolone from phenylhydrazine and ethyl acetoacetate. To obtain it quite pure, it must be boiled with barium carbonate, and the barium salt precipitated with hydrochloric acid. It crystallises in long, slender, silky needles, melts at 169—170°, is sparingly soluble in cold water and ether, readily in hot water and alcohol. It behaves as a base towards strong acids, forming a hydrochloride, which is at once decomposed by water, and may be heated with hydrochloric acid at 200°, or boiled with concentrated sulphuric acid, without undergoing decomposition. In its aqueous and alkaline solutions, it undoubtedly is at least partially converted into the free oximidobutyric acid, as the former has an acid reaction, and the solutions in soda and ammonia are not precipitated by acetic acid. *Barium oximidobutyrate*, $(C_4H_6O_3N)_2Ba + 2H_2O$, forms readily soluble, microscopic needles, and decomposes with explosion when heated. *Ammonium oximidobutyrate* may be crystallised from acetic acid solution, and forms silky, matted needles, which do not lose ammonia over sulphuric acid or at 100°; it melts at 206—207° with decomposition. With acetic anhydride or chloride, methylisoxazolone yields an acetyl derivative, which appears to have the composition $C_{10}H_{10}N_2O_4$, but is reconverted into the original oxazolone when boiled with water.

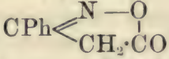
By the action of hydroxylamine on ethyl acetoacetate in neutral or acid solution, Westenberger obtained an oil which he regarded as ethyl oximidobutyrate; it is, however, at any rate, not a pure compound, and yields, on hydrolysis, a crystalline substance which is not oximidobutyric acid. This is scarcely soluble in the ordinary solvents, and has the composition $C_{20}H_{26}N_4O_7$, and is probably formed from ethyl oximidobutyrate according to the equation

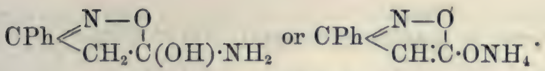
$$4C_6H_{11}NO_3 = C_{20}H_{26}N_4O_7 + 2C_2H_5\cdot OH + 3H_2O.$$

It dissolves without alteration in concentrated nitric acid, melts at 140°, and is resolved on hydrolysis into 2 mols. alcohol and 4 mols. methylisoxazolone.

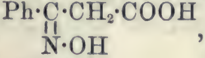
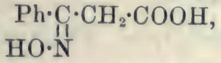
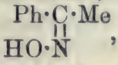
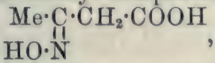
If the reaction with hydroxylamine be carried out in ammoniacal solution, an unstable product is obtained, which could not be purified, but may possibly be the hydroxamic acid of acetoacetic acid,

$$CH_2Ac\cdot C(OH)\colon N\cdot OH.$$

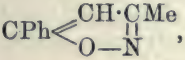
The author has further examined the action of hydroxylamine on ethyl benzoylacetate, and his results agree with those recently published by Claisen and Zedel (this vol., p. 468). One and the same product, namely, *phenylisoxazolone*,  $\mathrm{CPh}<\begin{matrix}\mathrm{N-O}\\ \mathrm{CH_2\cdot CO}\end{matrix}$, is obtained in acid, alkaline, and neutral solutions; the properties of this compound are given by Claisen and Zedel, but the author has also determined the molecular weight by Raoult's method in phenol solution, and finds it to agree with the above formula. It is much more stable in alkaline solution than methylisoxalone, and unites with ammonia, forming an additive compound having one of the following formulæ:—



$$\mathrm{CPh}<\begin{array}{l}\mathrm{N-O}\\ \mathrm{CH_2\cdot \overset{|}{C}(OH)\cdot NH_2}\end{array} \text{ or } \mathrm{CPh}<\begin{array}{l}\mathrm{N-O}\\ \mathrm{CH{:}\overset{|}{C}\cdot ONH_4}\end{array}.$$

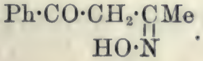
On exposure to moist air or over sulphuric acid, or by the action of acetic acid, it is reconverted into phenylisoxazolone. The latter is more readily acted on by acids than the methyl compound, as it is decomposed by concentrated hydrochloric acid at 120° into carbonic anhydride and acetophenonoxime. Concentrated sulphuric acid acts similarly, but the acetophenonoxime undergoes the Beckmann intramolecular change into acetanilide, which is further resolved into acetic and sulphanilic acids. The author regards it as probable that the anhydride first forms the acid  $\begin{array}{l}\mathrm{Ph\cdot C\cdot CH_2\cdot COOH}\\ \quad\ \|\\ \quad\ \mathrm{N\cdot OH}\end{array}$, which then in the stereo-isomeric form,  $\begin{array}{r}\mathrm{Ph\cdot C\cdot CH_2\cdot COOH},\\ \|\qquad\qquad\quad\\ \mathrm{HO\cdot N}\qquad\qquad\quad\end{array}$ loses carbonic anhydride, forming acetophenonoxime; the latter has already been shown to have the configuration  $\begin{array}{r}\mathrm{Ph\cdot C\cdot Me}\\ \|\qquad\\ \mathrm{HO\cdot N}\qquad\end{array}$, and the reason of the greater stability of the methyl compound may be due to the fact that the stereo-isomeride,  $\begin{array}{r}\mathrm{Me\cdot C\cdot CH_2\cdot COOH}\\ \|\qquad\qquad\quad\\ \mathrm{HO\cdot N}\qquad\qquad\quad\end{array}$, like all oximes in which the hydroxyl and methyl groups are adjacent, is either incapable of existence or exceptionally labile.

The researches of Claisen on the oximes of the β-diketones lead to similar results; thus the monoxime of benzoylacetone does not exist, but at once passes into the anhydride, *methylphenylisoxazole*,

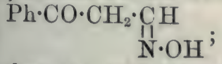


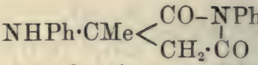
$$\mathrm{CPh}<\begin{array}{l}\mathrm{CH\cdot CMe}\\ \qquad\quad\|\\ \mathrm{O-N}\end{array},$$

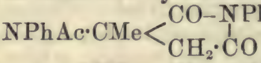
which shows that the oxime must have the configuration

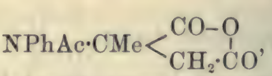


$$\begin{array}{r}\mathrm{Ph\cdot CO\cdot CH_2\cdot CMe}\\ \|\quad\\ \mathrm{HO\cdot N}\quad\end{array}.$$

On the other hand, benzoylacetaldoxime exists in the free state, and only yields phenylisoxazole with difficulty, namely, by boiling with acetic chloride, whilst with acetic anhydride, it readily yields cyanacetophenone $\mathrm{Ph\cdot CO\cdot CH_2\cdot CN}$, and must therefore have the configuration  $\begin{array}{l}\mathrm{Ph\cdot CO\cdot CH_2\cdot CH}\\ \qquad\qquad\quad\ \|\\ \qquad\qquad\quad\ \mathrm{N\cdot OH}\end{array}$; the action of acetic chloride is due to the fact that the hydrogen chloride set free converts the β-acetyl compound first formed into the α-acetyl compound, which then condenses to phenylisoxazole (compare this vol., p. 443). H. G. C.

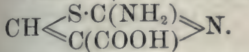
So-called Phenylketohydroxydimethylanilidotetrahydropyridinecarboxylic Lactone, a Contribution to the Knowledge of β-Anilidoglutaranil. By R. ANSCHÜTZ (*Annalen*, **261**, 138—151; compare Reissert, this vol., p. 567).—The author has proved that Reissert's phenylketohydroxydimethylanilidotetrahydropyridinecarboxylic lactone is β-anilidoglutaranil,  $\mathrm{NHPh{\cdot}CMe}<\begin{array}{l}\mathrm{CO{-}NPh}\\ \mathrm{CH_2{\cdot}CO}\end{array}$, (m. p. 131°). This compound is best prepared by heating β-anilidoglutaric acid (1 mol.) with aniline (1 mol.) at 160—180°; it forms monosymmetric crystals, $a : b : c = 0{\cdot}8093 : 1 : 0{\cdot}5128$, $\beta = 89° 18'$, and is identical crystallographically with the compound obtained by heating anilidoglutaric acid alone, as described by Reissert.

β-Acetanilidoglutaranil,  $\mathrm{NPhAc{\cdot}CMe}<\begin{array}{l}\mathrm{CO{-}NPh}\\ \mathrm{CH_2{\cdot}CO}\end{array}$, prepared by heating β-anilidoglutaranil (m. p. 131°) with acetic chloride at 100°, separates from dilute alcohol in crystals, melts at 168°, and is readily soluble in alcohol and acetone, but only sparingly in ether, and insoluble in water.

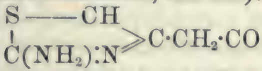
β-Acetanilidoglutaric anhydride,  $\mathrm{NPhAc{\cdot}CMe}<\begin{array}{l}\mathrm{CO{-}O}\\ \mathrm{CH_2{\cdot}CO}\end{array}$, is formed when β-anilidoglutaric acid is boiled with excess of acetic chloride for four to five hours. It separates from ether in well-defined, monosymmetric crystals, $a : b : c : = 0{\cdot}66654 : 1 : 0{\cdot}90258$, $\beta = 74° 42'$, melts at 136°, and is readily soluble in chloroform and benzene, but only sparingly in ether.

β-Acetanilidoglutaranilic acid, $\mathrm{NHPh{\cdot}CO{\cdot}CH_2{\cdot}CMe(NPhAc){\cdot}COOH}$, is obtained when the preceding compound is treated with the theoretical quantity of aniline in benzene, acetone, or ethereal solution; it separates from water in crystals containing 1 mol. H_2O, and from acetone in monosymmetric forms, $a : b : c = 0{\cdot}7973 : 1 : 0{\cdot}7642$, $\beta = 87° 34'$, melting at 140—141°. When boiled with acetic chloride, it is converted into β-acetanilidoglutaranil (m. p. 168—169°), which is identical with the acetyl derivative obtained by heating the so-called phenylketohydroxydimethylanilidotetrahydropyridinecarboxylic lactone with acetic chloride. F. S. K.

Thiazole Derivatives from Bromopyruvic Acids and from Ethyl Bromacetoacetate. By M. STEUDE (*Annalen*, **261**, 22—47). —The principal objects of this investigation were to determine the constitution of the so-called thiouvinuric acid described by Nencki and Sieber (Abstr., 1882, 501), and to ascertain the position of the bromine atom in ethyl bromacetoacetate (compare Hantzsch, Abstr., 1890, 1238).

Thiouvinuric acid can be obtained by treating thiocarbamide with monobromopyruvic acid, but it is most conveniently prepared from dibromopyruvic acid, as described by Nencki and Sieber (*loc. cit.*). The *ethyl* salt, $C_6H_8O_2N_2S$, is formed when ethyl bromopyruvate, prepared by brominating ethyl pyruvate in carbon bisulphide solution, is treated with thiocarbamide, an energetic reaction taking place; the product, which consists of the hydrobromide, is decomposed with ammonia and recrystallised from hot water. It melts at 173°, and is almost insoluble in cold water, but more readily in hot water, alcohol, and ether; on hydrolysis with boiling alcoholic potash, it yields thiouvinuric acid. The formation of the ethyl salt of thiouvinuric acid in this way proves that the acid is μ-amidothiazole-α-carboxylic acid,  $\mathrm{CH}{<}\substack{\mathrm{S{\cdot}C(NH_2)}\\ \mathrm{C(COOH)}}{>}\mathrm{N}$.

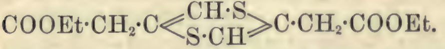
The thiazole derivatives, obtained by treating ethyl bromacetoacetate with thiocarbamide and thiacetamide respectively, are isomeric with the ethereal salts obtained from ethyl chloracetoacetate in like manner, but, on hydrolysis, they give acids which, when heated at a suitable temperature, are decomposed with evolution of carbonic anhydride, yielding μ-amido-α-methylthiazole and αμ-dimethylthiazole respectively. As these two thiazole derivatives are identical with the compounds obtained from ethyl chloracetoacetate in a similar manner, it follows that the original condensation products of ethyl bromacetoacetate are derivatives of thiazylacetic acid, and consequently that ethyl bromacetoacetate has the constitution $\mathrm{CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}COOEt}$ (compare Hantzsch, *loc. cit.*).

Ethyl μ-amidothiazylacetate,  $\begin{array}{l}\mathrm{S{-\!-}CH}\\ \mathrm{C(NH_2){:}N}\end{array}{>}\mathrm{C{\cdot}CH_2{\cdot}COOEt}$, is obtained when ethyl bromacetoacetate, prepared according to Duisberg's method (Abstr., 1882, 1193), is treated with thiocarbamide in alcoholic solution, and the resulting hydrobromide decomposed with ammonia. It separates from hot alcohol in yellowish, well-defined, seemingly monosymmetric crystals, melts at 94°, and is only sparingly soluble in cold water, but very readily in alcohol and ether; it dissolves freely in dilute acids, yielding salts which are soluble in alcohol. The free *acid*, $\mathrm{C_5H_6O_2N_2S}$, prepared by hydrolysing the ethereal salt with potash, melts at about 130°, and is sparingly soluble in water, but readily in alcohol; when warmed with acids, or heated alone for some time at its melting point, it is completely decomposed into carbonic anhydride and amidomethylthiazole.

Ethyl thiacetamidacetoacetate, $\mathrm{NH{:}CMe{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOEt}$, is formed, together with ethyl μ-methylthiazylacetate, when ethyl bromacetoacetate is treated with thiacetamide in alcoholic solution; on cooling the solution and stirring vigorously, the hydrobromide of ethyl thiacetamidacetoacetate is deposited in crystals, but if the solution is kept still and not cooled too quickly, no precipitation takes place, and the last-named compound is gradually but completely converted into ethyl methylthiazylacetate hydrobromide. Ethyl thiacetamidacetoacetate, prepared by decomposing the hydrobromide with sodium carbonate, crystallises in transparent rhombohedra, melts at 94°, and is decomposed by warm alkalis with evolution of ammonia; attempts to convert the pure compound into ethyl methylthiazylacetate were unsuccessful, although it was proved by various experiments that it is, in fact, an intermediate product in the formation of the thiazole derivative.

Ethyl methylthiazylacetate, $\mathrm{C_8H_{11}O_2NS}$, obtained by decomposing the hydrobromide with sodium carbonate, is a colourless liquid boiling at 238—240°; the *platinochloride*, $\mathrm{(C_8H_{11}O_2NS)_2,H_2PtCl_6}$, is a yellow, crystalline compound melting at 89°. The free *acid*, $\mathrm{C_6H_7O_2NS}$, prepared by treating the ethereal salt with moderately concentrated potash at the ordinary temperature, crystallises in small needles, melts at 121°, and is only sparingly soluble in water, but more readily in alcohol and ether; when the acid is distilled, it is completely converted into $\alpha\mu$-dimethylthiazole with evolution of carbonic anhydride.

Ethyl γ-thiacetoacetoacetate, $COMe{\cdot}S{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, is precipitated as an oil when ethyl thiacetamidacetoacetate hydrobromide is warmed with water. It boils at 155° under a pressure of 15 mm., is insoluble in dilute acids, and only sparingly soluble in water, but miscible with alcohol and ether; it is acted on by concentrated nitric acid with almost explosive violence, yielding small quantities of a crystalline compound, which is free from sulphur and explodes when heated.

A compound of the composition $C_6H_8O_2S$ is formed, together with acetic acid, when ethyl thiacetoacetoacetate is carefully mixed with concentrated sulphuric or hydrochloric acid, and, after cooling and adding a little water, the product is deposited in crystals; the same compound is produced in small quantities when ethyl bromacetoacetate is shaken with a 2 per cent. solution of sodium hydrosulphide. It separates from alcohol in slender needles, melts at 168°, and is moderately easily soluble in alcohol and ether, but insoluble in water and acids; its physical properties indicate a high molecular weight, and its constitution is probably represented by the formula  $COOEt{\cdot}CH_2{\cdot}C\!<\!\begin{smallmatrix}CH{\cdot}S\\S{\cdot}CH\end{smallmatrix}\!>\!C{\cdot}CH_2{\cdot}COOEt$. When hydrolysed with alcoholic potash, it yields a crystalline potassium salt, from which a colourless, crystalline acid, melting at about 140°, is obtained on treatment with hydrochloric acid.

F. S. K.

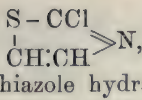
Attempts to Prepare Hydrothiazole Derivatives. By P. Schatzmann (*Annalen*, **261**, 1—21).—Various experiments were made with the object of synthesising hydrothiazole derivatives, but without success. When glycol chlorhydrin is warmed with thiocarbamide, the product extracted with water, and the solution evaporated, small, hygroscopic crystals of hydroxyethylthiocarbamide hydrochloride, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}C(NH){\cdot}NH_2,HCl$, are deposited; attempts to convert this substance into dihydroamidothiazole were unsuccessful.

Ethylenedithiocarbamide hydrobromide is formed when ethylene bromide (1 mol.) is treated with thiocarbamide (1 mol.). The free *base*, $C_4H_{10}S_2N_4$, prepared by digesting the salt with silver oxide, forms grey crystals, and is readily soluble in water, alcohol, ether, and acids.

Dimethylthiazole is completely decomposed on treatment with sodium in alcoholic solution, the products being ethylamine and propyl mercaptan; other reducing agents, such as zinc and hydrochloric acid, zinc-dust and acetic acid, have no action on dimethylthiazole.

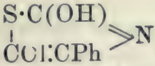
Phenylmethylthiazole is not acted on by sodium and alcohol, or by concentrated ammonia at 280°.

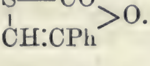
An orange-yellow compound is formed when amidothiazole hydrochloride is treated with sodium nitrite in well-cooled aqueous solution; this substance is doubtless either diazothiazole hydrate or nitrosoimidothiazoline, as is shown by its behaviour with halogen acids, but it was not analysed on account of its instability.

μ-Chlorothiazole,  $\begin{array}{l}\mathrm{S-CCl}\\ \vert\\ \mathrm{CH{:}CH}\end{array}\!>\!\mathrm{N}$, is obtained when a concentrated solution of amidothiazole hydrate is treated with the theoretical quantity of sodium nitrite in the cold and then boiled with excess of concentrated hydrochloric acid. It is a colourless oil, specifically heavier than water, boils at 144—144·5°, and is readily volatile with steam; it is only sparingly soluble in water, but miscible with alcohol and ether in all proportions. It dissolves freely in concentrated mineral acids, but its salts are very unstable. The *platinochloride*, $(C_3H_2NSCl)_2,H_2PtCl_6$, is a yellow, crystalline, unstable compound, sparingly soluble in alcohol.

μ-Bromothiazole, C_3H_2SNBr, prepared in like manner, is a colourless liquid, boils at 171°, and is very similar to the corresponding chloro-derivative in all respects. The *platinochloride*, $(C_3H_2SNBr)_2,H_2PtCl_6$, is unstable, and melts at 197° with decomposition. The corresponding iodo-derivative could not be obtained; the chloro- and bromo-compounds just described are readily acted on by zinc-dust and acetic acid, being converted into thiazole.

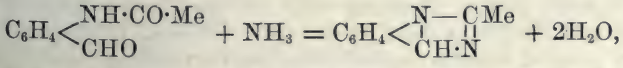
Phenyldiazothiazole hydrate, or *phenylnitrosoimidothiazoline*, $C_9H_7N_3SO$, can be obtained by treating phenylamidothiazole hydrobromide with sodium nitrite in aqueous solution; it is a yellow, unstable compound, and is decomposed by boiling hydrochloric acid, yielding benzoic acid.

Phenylhydroxychlorothiazole,  $\begin{array}{l}\mathrm{S\cdot C(OH)}\\ \vert\\ \mathrm{CCl{:}CPh}\end{array}\!>\!\mathrm{N}$, is formed in small quantity when phenylhydroxythiazole is melted with phosphorus pentachloride, but the principal product is a substance melting at 98°, the nature of which could not be determined; phenylchlorhydroxythiazole separates from ether in yellowish crystals, melts at 206°, and is soluble in soda.

When carbaminethiacetophenone, $COPh\cdot CH_2\cdot S\cdot CO\cdot NH_2$, an intermediate product obtained in the preparation of phenylhydroxythiazole from acetophenone thiocyanate is oxidised with boiling dilute nitric acid, it is converted into a yellow, crystalline compound melting at 75°; this substance has the composition $C_9H_6SO_2$, and its constitution is probably expressed by the formula  $\begin{array}{l}\mathrm{S-\!\!-CO}\\ \vert\\ \mathrm{CH{:}CPh}\end{array}\!>\!\mathrm{O}$.

F. S. K.

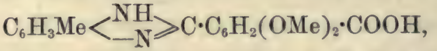
Pheno-2′-methylmetadiazine (2′-Methylquinazoline). By A. Bischler (*Ber.*, **24**, 506—508).—By the action of alcoholic ammonia at 100° on acetylorthamidobenzaldehyde, the following reaction takes place:—



$$C_6H_4<\begin{array}{l}NH\cdot CO\cdot Me\\ CHO\end{array} + NH_3 = C_6H_4<\begin{array}{l}N-CMe\\ \vert\quad\;\; \Vert\\ CH\cdot N\end{array} + 2H_2O,$$

pheno-2′-methylmetadiazine being formed. The oily product is distilled in a current of steam, the distillate extracted with ether, and the ethereal solution evaporated and fractionated. *Pheno-2′-methylmetadiazine* distils at 235° under 713 mm. pressure, solidifies after a time, and then melts at 35·5°. It is hygroscopic, and forms a crystalline *hydrochloride*, $C_9H_8N_2,HCl$, and a yellow, crystalline *platinochloride*, $(C_9H_8N_2)_2,H_2PtCl_6$. The above reaction is quite general, and is being thoroughly investigated. H. G. C.

Action of Orthodiamines on Orthaldehydobenzoic Acids. By A. Bistrzycki (*Ber.*, **24**, 627—630; compare Abstr., 1890, 969). —*Toluyleneamidinedimethyloxybenzenylcarboxylic acid*,



$$C_6H_3Me{<}\begin{smallmatrix}NH\\ —N\end{smallmatrix}{\geqslant}C\cdot C_6H_2(OMe)_2\cdot COOH,$$

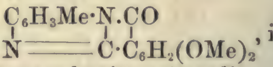
is formed when opianic acid (2 mols.) is boiled with metaparatoluylenediamine (1 mol.) in 80 per cent. alcoholic solution. It crystallises from 80 per cent. acetic acid in small, colourless needles, melts and decomposes at about 234° when quickly heated, and is readily soluble in hot glacial acetic acid, but only moderately in chloroform, very sparingly in alcohol, and is almost insoluble in ether and light petroleum; it dissolves freely in dilute mineral acids and in alkalis. The *calcium* salt, $(C_{17}H_{15}N_2O_4)_2Ca$, is only sparingly soluble in hot water.

Bromotoluyleneamidinedimethoxybenzenylcarboxylic acid,

$$C_{17}H_{15}N_2O_4Br,$$

prepared from opianic acid and metabromometaparatoluylenediamine in like manner, crystallises from alcohol in small, flat, colourless needles, melts at 240° with decomposition, and resembles the preceding compound in general behaviour, but is more sparingly soluble.

Toluylenedimethoxyphthalamidone,

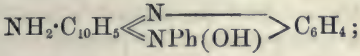


$$\begin{array}{l}C_6H_3Me\cdot N.CO\\ \;|\qquad\quad\;\;|\quad|\\ N\text{———}C\cdot C_6H_2(OMe)_2\end{array},$$

is formed when toluyleneamidinedimethoxybenzenylorthocarboxylic acid is boiled with acetic anhydride. It crystallises from benzene or alcohol in slender, yellow needles, melts at 228° with decomposition and previous softening, and is readily soluble in hot benzene, alcohol, glacial acetic acid, chloroform, and acetone, but only sparingly in ether, and insoluble in light petroleum; its solution in benzene shows a green fluorescence. It dissolves in concentrated sulphuric acid with an orange coloration, but on adding water, and heating, the solution becomes colourless. F. S. K.

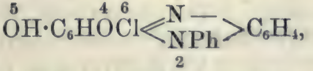
Relations of the Eurhodines to the Indulines and Saffranines. By F. Kehrmann and J. Messinger (*Ber.*, **24**, 584—592; compare Abstr., 1890, 1265).—Rosindone is obtained by mixing hydroxynaphthaquinone and phenylorthophenylenediamine dissolved in molecular proportion in alcohol at the ordinary temperature; it melts at 261—262°, and is identical with the compound obtained by O. Fischer and E. Hepp from rosinduline (Abstr., 1890, 908). The authors propose to term the ketoinduline derivatives "indulones," so as to avoid confusion with the ketoindene derivatives; "rosindone" of Fischer and Hepp would, therefore, become the "*rosindulone*" or naphthaphenindulone corresponding with rosinduline or naphthaphheninduline.

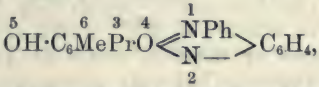
Rosinduline is prepared in a similar manner to the indulone, by heating hydroxynaphthaquinonimide and phenylorthophenylenediamine with alcohol and a little glacial acetic acid at 100° under pressure; the yield is 40—60 per cent. of the quinonimide taken. It is suggested that the salts of rosinduline are derived from an unstable ammonium base with the formula



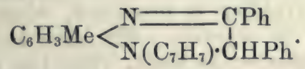
$$NH_2{\cdot}C_{10}H_5<\begin{matrix}N\text{———}\\ NPh(OH)\end{matrix}>C_6H_4;$$

this would account for their similarity in properties to the saffranines.

Chlorhydroxyphenindulone,  $\overset{5}{O}H{\cdot}C_6H\overset{4}{O}\overset{6}{C}l<\begin{matrix}\overset{1}{N}\text{—}\\ \underset{2}{NPh}\end{matrix}>C_6H_4$, prepared from chlorodihydroxyquinone and phenylorthophenylenediamine, crystallises from glacial acetic acid in chocolate-coloured, highly lustrous plates, melts at 270—272° with decomposition, and is sparingly soluble in ordinary media, but dissolves in sulphuric acid with a green colour, and is precipitated unchanged on dilution; the solution in dilute soda or concentrated ammonia is red. The *benzoyl derivative* crystallises from alcohol in bronze, lustrous, concentrically grouped needles melting at 234—235°.

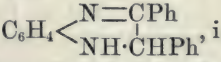
Hydroxythymophenindulone,  $\overset{5}{O}H{\cdot}C_6\overset{6}{M}e\overset{3}{P}r\overset{4}{O}<\begin{matrix}\overset{1}{NPh}\\ \underset{2}{N}\text{—}\end{matrix}>C_6H_4$, obtained from dihydroxythymoquinone and phenylorthophenylenediamine, crystallises from alcohol in ruby-red plates and prisms, melts at 174—175°, and gives an olive-green colour with sulphuric acid. No other condensation product could be detected. J. B. T.

A New Class of Fluorescent Colouring Matters of the Quinoxaline Series. By O. FISCHER (*Ber.*, **24**, 719—723).—When orthamidoditolylamine is fused with benzoïn, 2 mols. of water are eliminated, and a dihydroquinoxaline derivative of the following constitution formed:—

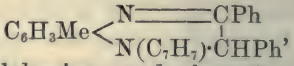


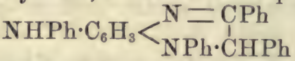
$$C_6H_3Me<\begin{matrix}N\text{═══}CPh\\ \qquad\quad\ |\\ N(C_7H_7){\cdot}CHPh\end{matrix}.$$

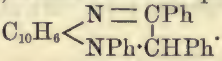
The reaction is a general one, and all the dihydroquinoxaline derivatives thus obtained are colouring matters with a yellowish- or brownish-green fluorescence, whilst the corresponding simple quinoxalines have no similar properties.

Diphenyldihydroquinoxaline,  $C_6H_4<\begin{matrix}N\text{═}CPh\\ \quad\ \ |\\ NH{\cdot}CHPh\end{matrix}$, is prepared by heating orthodiamidobenzene and benzoïn, in molecular proportions, in a sealed tube at 170° for three hours, as in the presence of air large quantities of diphenylquinoxaline are formed. It crystallises in thick, dark-yellow, prismatic crystals, certain faces of which reflect a beautiful, green light, melts at 148—149°, and is readily soluble in benzene and hot alcohol, sparingly in ether and light petroleum, insoluble in water; the solutions in ether and benzene show a beautiful, yellowish-green fluorescence, and colour paper an intense yellow.

It is a feeble base, forming orange-red salts, which are dissociated by water, distils unchanged in small quantities, and is oxidised by ferric chloride to diphenylquinoxaline.

Diphenyltolyltoludihydroquinoxaline,  $C_6H_3Me<\begin{array}{l}N=\!=CPh\\ N(C_7H_7)\cdot CHPh\end{array}$, is obtained by heating orthamidoditolylamine and benzoïn, in molecular proportion, at 180° for several hours; it crystallises from light petroleum in pale-yellow, thick prisms, certain faces of which have a green reflex. Its solubility and fluorescence are the same as with the diphenyl derivative, but it dissolves in mineral acids with a magenta colour. The formula $C_{28}H_{24}N_2$ has been confirmed by a determination of the molecular weight by Raoult's method.

Diphenyl-1 : 3 : 4-triamidobenzene (Abstr., 1890, 614) reacts with benzene at 160°, forming a yellow, fluorescent compound, having the constitutional formula  $NHPh\cdot C_6H_3<\begin{array}{l}N=CPh\\ NPh\cdot CHPh\end{array}$; it crystallises from absolute alcohol in beautiful, greenish-yellow, lustrous plates, melts at 223°, and is readily soluble in benzene and chloroform, sparingly in alcohol, ether, and light petroleum, the yellow solutions showing a deep green fluorescence. Its salts have a pink colour.

β-Phenylorthonaphthylenediamine also yields a similar colouring matter with benzoïn at 200°, which crystallises from alcohol in deep-yellow plates or needles, melts at 163—164°, is readily soluble in ether and benzene, but only sparingly in alcohol and light petroleum, the solutions having a greenish-yellow fluorescence. It yields deep-red salts, which are decomposed by water. It has the constitutional formula  $C_{10}H_6<\begin{array}{l}N=CPh\\ NPh\cdot CHPh\end{array}$.

H. G. C.

Alkaloïds of Belladonna. By O. Hesse (*Annalen*, **261**, 87—107; compare this vol., p. 228).—Atropamine, $C_{17}H_{21}NO_2$, is easily isolated from the roots of *Atropa belladonna* by dissolving the crude mixture of alkaloïds in acetic acid, and adding sodium chloride to the solution until a permanent turbidity is produced, when atropamine hydrochloride is deposited in crystals. The free base is obtained in the form of a colourless, semi-solid resin, when the pure hydrochloride is decomposed with ammonia, the base extracted with ether, the ethereal solution washed with ammonia and water consecutively, and then evaporated over sulphuric acid; it is very readily soluble in benzene, but only sparingly in light petroleum and water. Its alcoholic solution has a bitter taste, and turns red litmus-paper blue, but is without action on phenolphthaleïn-paper. The *hydrochloride*, $C_{17}H_{21}NO_2,HCl$, crystallises from boiling water in colourless plates, melts at 236°, and is moderately easily soluble in hot water, but only sparingly in alcohol and acetone, and insoluble in ether. The *platinochloride*, $(C_{17}H_{21}NO_2)_2,H_2PtCl_6$, forms small, reddish-yellow needles, and is only sparingly soluble in cold water. The *aurochloride*, $C_{17}H_{21}NO_2,HAuCl_4$, crystallises in small, lustrous plates melting at 112°. The *mercurochloride* forms small, colourless plates, and is moderately easily soluble in boiling water. The *hydrobromide*, $C_{17}H_{21}NO_2,HBr$, crystallises in colourless plates, melts at 230°, and is readily soluble in hot water. The *hydriodide*, *nitrate*, normal *sulphate*, and *picrate* are crystalline.

When atropamine is dissolved in cold concentrated sulphuric acid, or boiled with barium hydroxide or dilute hydrochloric acid, or when its hydrochloride is moistened with hydrochloric acid and exposed to sunlight, it is converted into belladonnine, $C_{27}H_{21}NO_2$, an alkaloïd which has been previously investigated by Kraut (Abstr., 1880, 410), Merling (Abstr., 1884, 1055), Ladenburg and Roth (Abstr., 1884, 761), and others. On prolonged boiling with alcoholic barium hydroxide or with moderately concentrated hydrochloric acid, atropamine is decomposed into a volatile base and various acids, amongst which is α-isatropic acid (m. p. 239°). The volatile base seems to be identical with pseudotropine; it is a crystalline, deliquescent compound, very readily soluble in alcohol and water, but very sparingly in ether. The *platinochloride*, $(C_8H_{15}NO)_2,H_2PtCl_6$, melts at 186° with decomposition, and differs in crystalline form from the corresponding salt of tropine; the aurochloride crystallises in plates, and melts at 195—198° with decomposition.

When atropamine is heated at 100° with fuming hydrochloric acid, it yields atropic acid (m. p. 107°), identical with the compound obtained from atropine under the same conditions.

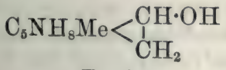
The author's experiments show that atropamine stands in the same relationship to hyoscine that apoatropine does to atropine.

F. S. K.

Tropinic Acid and Oxidation Products of Dextro- and Lævo-ecgonine and of Tropine. By C. LIEBERMANN (*Ber.*, **24**, 606—617; compare Abstr., 1890, 1449).—The acid $C_7H_{11}NO_3$, obtained by the oxidation of lævo-ecognine, is termed *ecgonic acid*, and is much more soluble in water than tropinic acid; it is lævorotatory, $[\alpha]_D = -43{\cdot}2°$, and is also formed, together with tropinic acid, by the oxidation of dextro-ecgonine and of tropigenine. On oxidising tropine, optically inactive tropinic acid is obtained, together with a compound which exhibits all the properties of ecgonic acid, except that it melts at 90° instead of at 117°; this may, however, be due to the presence of some impurity. *Ethyl ecgonate*, $C_7H_{10}EtNO_3$, is a colourless, viscid liquid.

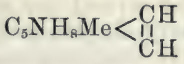
Tropinic acid is bibasic; its rotatory power is $[\alpha]_D = +14{\cdot}8°$; the silver salt is not well adapted for analysis; the *cupric salt*, obtained by crystallisation from water, has the formula $C_8H_{12}NO_4{\cdot}CuOH$; on heating this for some time at 165—170°, a molecule of water is eliminated, and the *normal salt*, $C_8H_{11}NO_4Cu$, remains as a pale-blue powder. *Methyl tropinate*, $C_8H_{11}Me_2NO_4$, and *ethyl tropinate*, $C_8H_{11}Et_2NO_4$, are colourless, viscid liquids, insoluble in water.

These results point to the incorrectness of Ladenburg's formula for tropine, and of Einhorn's formula for ecgonine, since each of these has only one side chain linked to the pyridine nucleus; the author adopts Merling's formulæ for this group of compounds, the relative position of the side chains being as yet undetermined :—



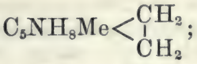
$$C_5NH_8Me<\begin{array}{l}CH\cdot OH\\ \vert\\ CH_2\end{array};$$

Tropine.



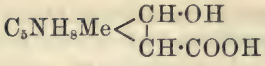
$$C_5NH_8Me<\begin{array}{l}CH\\ \Vert\\ CH\end{array};$$

Tropidine.



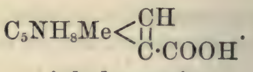
$$C_5NH_8Me<\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array};$$

Hydrotropidine.



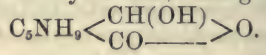
$$C_5NH_8Me{<}\begin{array}{l}CH{\cdot}OH\\ \vert\\ CH{\cdot}COOH\end{array}$$

Ecgonine.



$$C_5NH_8Me{<}\begin{array}{l}CH\\ \Vert\\ C{\cdot}COOH\end{array}.$$

Anhydroecgonine.

Ecgonic acid is probably an aldehyde acid, analogous to opianic acid, and may have the formula  $C_5NH_9{<}\begin{array}{l}CH(OH)\\ CO\text{——}\end{array}{>}O$.

J. B. T.

Cytisine. By A. Partheil (*Ber.*, **24**, 634—640; compare this vol., p. 231, and Buchka and Magalhaēs, this vol., p. 587). Cytisine melts at 152—153° (uncorr.) and can be crystallised from hot chloroform; when treated with hydriodic acid, it does not yield methyl iodide; its molecular weight was determined, in aqueous solution, by Raoult's method, with results agreeing well with the molecular formula $C_{11}H_{14}N_2O$. The *hydrobromide*, $C_{11}H_{14}N_2O,HBr$, crystallises from cold water in small, colourless needles, containing 1 mol. H_2O. The *hydriodide* with 1 mol. H_2O, *nitrate*, $C_{11}H_{14}N_2O,HNO_3 + H_2O$, and *sulphate*, $(C_{11}H_{14}N_2O)_2,H_2SO_4 + H_2O$, crystallise in colourless needles. The *methiodide*, $C_{11}H_{14}N_2O,MeI$, prepared by heating cytisine with methyl iodide at 100°, crystallises from dilute alcohol in needles containing 2 mols. H_2O, and is readily soluble in water. The *ethiodide*, $C_{11}H_{14}N_2O,EtI$, separates from alcoholic ether in almost colourless crystals. When cytisine is oxidised with alkaline potassium permanganate, ammonia is evolved; under the same conditions, the methiodide is decomposed with evolution of methylamine.

A direct comparison of ulexine, prepared from the seeds of *Ulex europæus*, with cytisine proved that the two compounds are identical (compare Gerrard and Symons, this vol., p. 334). F. S. K.

Cytisine. By K. Buchka and A. Magalhaēs (*Ber.*, **24**, 674—680; compare preceding abstract).—Measurements of the electrical conductivity of aqueous solutions of cytisine showed that it is only a feeble base.

Methylcytisine hydriodide (*cytisine methiodide*), $C_{12}H_{16}N_2O,HI$, melts at 253·5°, and is decomposed by hot potash yielding methylcytisine; this base separates from chloroform in crystals and melts at 245°. The *hydrochloride*, $C_{12}H_{16}N_2O,2HCl + 1\frac{1}{2}H_2O$, forms colourless crystals, melts at 249—250°, and is readily soluble in water. The *aurochloride*, $C_{12}H_{16}N_2O,HAuCl_4$, is a yellow, crystalline compound melting at 196°.

Acetylcytisine, $C_{13}H_{16}N_2O_2$, prepared by heating cytisine with acetic anhydride, separates from alcohol in almost colourless crystals, melts at 208°, and is decomposed by alkalis.

Nitrosocytisine, $C_{11}H_{13}N_3O_2$, is obtained when an aqueous solution of cytisine hydrochloride is treated with sodium nitrite in the cold; it crystallises in colourless needles, melts at 174°, and gives Liebermann's reaction very distinctly.

The authors compared several derivatives of cytisine with the corresponding derivatives of ulexine, prepared from the seeds of *Ulex europæus*; the result of the comparison was in favour of the identity of the two bases, but, on the other hand, when ulexine is heated with methyl iodide, it yields a compound melting at 290°, whereas cytisine methiodide melts at 253·5°. F. S. K.

Aspergillin, a Vegetable Hæmatin. By G. LINOSSIER (*Compt. rend.*, **112**, 489—492).—The spores of *Aspergillus niger*, when treated with very dilute ammonia, yield a dark-coloured solution from which a slight excess of hydrochloric acid throws down *aspergillin* as a black, bulky, flocculent precipitate. When dried over sulphuric acid at the ordinary temperature and powdered, it closely resembles hæmatin in appearance, and its general resemblance to this substance justifies the name "vegetable hæmatin," although whether the two substances have similar functions has yet to be determined.

Aspergillin is almost insoluble in water, alcohol, and neutral solvents, and is insoluble in dilute mineral acids, but dissolves in dilute acetic acid. It dissolves easily even in dilute solution of alkaline hydroxides, alkaline carbonates, and certain salts which have an alkaline reaction such as borax and disodium hydrogen phosphate. As in the case of hæmatin, its ammoniacal solution is precipitated by barium hydroxide. When freshly precipitated, aspergillin forms a colloïdal semi-solution with water, which is converted into a perfect solution by alkalis, but is precipitated by acids and certain neutral salts. Heat reduces the solubility in various solvents, and if heated for some hours at 180°, it becomes insoluble in alkalis. When heated in presence of air, aspergillin evolves an odour of burnt horn, and, like hematin, leaves a residue of ferric oxide.

Acid solutions are brown (green in thin layers) and alkaline solutions are reddish-brown; they exert a general absorption throughout the spectrum, increasing in intensity, though not continuously, from the red to the violet. An ammoniacal solution seems to undergo no change even after prolonged exposure to light. Sodium hyposulphite reduces solutions of aspergillin and the product absorbs oxygen with great energy when exposed to air, the colour very rapidly changing back from golden-yellow to brown. C. H. B.

Physiological Chemistry.

Effect of Certain Organic Acids on the Digestion of Proteïds. By A. STUTZER (*Landw. Versuchs-Stat.*, **38**, 257—261).—The action of hydrochloric and various organic acids on the digestion of proteïds by pepsin has been carefully studied, the substance experimented on being cotton-seed meal; three different strengths of acid solution were employed, namely, 0·05, 0·1, and 0·20 per cent. The relative activities of acid of 0·1 per cent. as calculated on the amount of dissolved nitrogen was as follows:—Hydrochloric, 62; formic, 30; acetic, 7; propionic, 1; butyric, 7; lactic, 39; malic, 33; tartaric, 34; citric, 27. E. W. P.

Effect of Salt on Digestion. By A. STUTZER (*Landw. Versuchs-Stat.*, **38**, 262—267).—The effects of sodium chloride on digestion known hitherto are, solution of albumin in aqueous liquids, increased excretion of stomach juices (pepsin), and the increased rapidity of the diffusion of liquids. The questions which the author strives to answer are: Will pepsin dissolve as much albumin when sodium chloride is present as when it is absent; and has sodium chloride a specific action on the pepsin, or on the hydrochloric acid, or on both? The solutions employed were: (1) water; (2) water and sodium chloride; (3) water and hydrochloric acid; (4) water, sodium chloride, and hydrochloric acid; (5) acidified stomach juice; (6) sodium chloride. The material acted on was cotton-seed meal soaked in chloroform-water, the temperature 40°, the time 30 minutes. Results: Salt alone has no appreciable action. Hydrochloric acid even in 0·05 per cent. solution has a very considerable solvent power, provided sodium chloride be present to the extent of only 0·25 per cent. Increase of sodium chloride means decrease of solvent action; increase of acid to 0·2 per cent. with small amount of salt, 0·25 per cent., is accompanied by increase of solvent power (53—71), but 1 per cent. of sodium chloride hinders the action of the acid. 1 per cent. of salt causes pepsin to dissolve more albumin than 0·25 or 0·5 per cent. of sodium chloride in the presence of acid. Pepsin solutions with salt added are capable of dissolving more albumin than when salt is absent; the most advantageous conditions under which salt acts are when 0·05 or 0·10 per cent. of hydrochloric acid is present. E. W. P.

Influence of Heat on the Digestibility of Fodder. By A. STUTZER (*Land. Versuchs-Stat.*, **38**, 267—276).—Wheaten bran: A temperature of 100° reduces the solubility of the proteïds; hydrochloric acid (without pepsin) has scarcely any action on boiled bran, whilst on bran heated in the dry state to 98°, its action is but slightly reduced. With reference to bread and meal, it appears that the process of baking the flour has but a small effect on the digestibility of the nitrogenous matter, this being rendered slightly less soluble, the proteïds of the crust of bread being less digestible than those of the crumb. Hydrochloric acid readily dissolves the proteïds of flour, but is almost without action on those contained in bread; whilst water alone dissolves four times the amount out of meal that it does out of bread.

The proteïds of earth-nut cake become less soluble in water after having been exposed to a moist or dry heat. Hydrochloric acid (0·05 per cent.) has no solvent power on this meal when it has been boiled with water, but a dry heat has no influence on the solubility of the proteïds. Dry or moist heat reduces the solubility in acid stomach juice. From these experiments, it would appear that fodders are not rendered more digestible by heat as regards the proteïd matter, but possibly may be so as regards the cellulose.

E. W. P.

Influence of Oil or Fat on the Digestibility of Proteïds. By A. STUTZER (*Landw. Versuchs-Stat.*, **38**, 277—279).—The presence of fat or oil in fodders (cocoa-nut cake, &c.) appears to have but a very slight reducing action on the solubility of proteïds in water or hydrochloric acid (without pepsin), and the differences observed when pressed and unpressed meals are submitted to the solvent action of pepsin are so slight, that the author considers that these differences must be attributed to errors of observation. E. W. P.

Effect of Increasing the Proteïds in Food Rations of Grown Animals. By E. KERN and H. WATTENBERG (*Bied. Centr.*, 1891, 77—87).—The experiments described were conducted in the year 1879, and consisted in feeding two 3½-year-old sheep with an ordinary ration of hay and crushed barley, and in addition, during the first three periods (July 14—Sept. 24), with increasing quantities of proteïd in the form of conglutin (70—210 grams), and in the following two periods (Sept. 15—Oct. 25) with decreasing quantities in the form of flesh meal (152—76 grams) from which all fat had been removed. The sheep were kept in Pettenkofer's respiration apparatus, and all excretion products were collected and measured.

The mean daily growths of crude wool were in the one case 11·33 grams, in the other 13·71; a table of digestion coefficients during all periods is given, and it is pointed out that the sum of the amounts of crude fibre and of non-nitrogenous extractive matters digested closely approaches to the amount of non-nitrogenous extractive in the *original* food. Period I, extractive in food, 472 grams; digested food fibre, 141 grams; digested extractive, 324 = 465 grams. Do. do. sheep II, 473 grams. In Period V, the results are respectively 459, 447·8, 455.

The percentage of hippuric acid was lowered as the proteïds in the food were increased, but resumed its original quantity during the periods when the proteïds were decreased; there was also an increase in flesh with increase of proteïds ingested.

As regards products of respiration during Period I (no extra nitrogen), there was expired 727·4 grams of carbonic anhydride, of which 56·4 per cent. was produced during the day—this quantity rose as the food increased in richness; and in Period IV, we find 815·7 grams of carbonic anhydride expired, of which 56·6 per cent. appeared in the day-time. Finally, during the last period, when all additional nitrogen was withdrawn, the total carbonic anhydride was 676·0 grams, of which 56·7 per cent. was obtained during the day.

Although the results were not as satisfactory as could have been desired, yet the authors consider that an increase of proteïds in food is accompanied by a decrease in the excretion of methane. Other points examined, such as the formation of fat and flesh from a known quantity of proteïds, have not led to any satisfactory results.

E. W. P

Oxygen in the Blood of Animals at Great Altitudes. By VIAULT (*Compt. rend.*, **112**, 295—298).—The author has previously found that one of the first effects produced on animals which are transferred to great altitudes from the low levels to which they are accustomed is a considerable increase in the number of red corpuscles in the blood. He has now determined, at the place, the quantity of oxygen in the blood of animals on the upper slopes of the Cordilleras. Sheep, at a height of 4392 metres, and a pressure of 450 mm., gave 13·16 c.c.

and 13·30 c.c. of oxygen per 100 c.c. of blood. A dog, at a height of 3724 metres, and a pressure of 485 mm., gave 18·26 c c. of oxygen per 100 c.c. The maximum absorptive power of the blood in these three cases was 16·0, 17·0, and 25 c.c. respectively. Similar results were obtained at the summit of the Pic du Midi, and it follows that at great altitudes the proportion of oxygen in the blood of animals is practically the same as at low levels. It would seem that the greater rarefaction of the oxygen is compensated by the greater degree of subdivision of the red corpuscles and their consequent greater absorptive activity.

C. H. B.

Increase in the Quantity of Hæmoglobin in the Blood according to the Conditions of Existence. By A. Müntz (*Compt. rend.*, **112**, 298—301).—Ordinary rabbits were taken from the plain in August, 1883, and were transferred to the summit of Pic du Midi, at a height of 2877 metres, and a pressure of 540 mm. They seemed to acclimatise at once, and fed and multiplied in a normal manner. In August, 1890, some of the rabbits, born on the Pic, and descendants of those transported from the plain many generations before, were killed, and their blood compared with that of rabbits living on the plain :—

	Sp. gr.	Solids per cent.	Iron in 100 grams.	Oxygen absorbed by 100 c.c.
Rabbits from Pic du Midi	1060·1	21·88	70·2 mgr.	17·28 c.c.
Rabbits from the plain..	1046·2	15·75	40·3 ,,	9·56 ,,

It follows that, after many generations, the blood of animals living at great altitudes becomes richer in hæmoglobin, and thus acquires a greater absorptive power which compensates for the rarefaction of the oxygen.

It seems, however, that a comparatively short time is required to bring about this change. The blood of sheep grazing at a height of 2300—2700 metres, to which they had been transferred from the plain six weeks before, was compared with that of similar sheep that had remained in the valley :—

	Sp. gr.	Solid matter per cent.	Iron in 100 grams.	Oxygen absorbed by 100 c.c.
Sheep on the mountain	1053·2	18·19	60·4 mgr.	17·47 c.c.
Sheep in the valley	1038·0	13·58	32·5 ,,	7·32 ,,

The blood undergoes the same change in the process of fattening :—

	Sp. gr.	Solid matter per cent.	Iron in 100 grams.	Oxygen absorbed. by 100 c.c.
Fat sheep	1058·0	20·33	57·0 mgr.	16·4 c.c.
Ordinary sheep .	1038·0	13·60	33·0 ,,	7·7 ,,

C. H. B.

Effect of Medicines, and especially of Valerian Extract, on the Destruction of Dextrose in the Blood. By L. Butte (*Compt.

rend. **112**, 347—350).—The dextrose was estimated by the fermentation method with the use of a mercurial pump (Quinquaud and Gréhant). Sodium hydrogen carbonate or morphine retards the destruction of dextrose in the blood, but curarine accelerates it. Valerian extract retards the destruction very considerably when added to freshly-drawn blood, and also when injected into the left femoral vein of a dog. C. H. B.

Isolation of the Glycolitic Ferment of the Blood. By R. Lépine and Barral (*Compt. rend.*, **112**, 411—412).—Fresh dog's blood was defibrinated and placed in a powerful centrifugal machine; the serum thus separated was found to have very little glycolytic power. The separated corpuscles were treated with a volume of salt water equal to the original serum, and the process of separation was repeated; the salt solution contained much less albumin than the serum, but its glycolytic power was much greater. A second treatment with salt water gave a liquid with very little albumin, but with still greater glycolytic power. It follows, therefore, that the destruction of glucose is not due, as Arnaud has supposed, to some action of living blood albumin; the results point, in fact, to the existence of a soluble ferment. C. H. B.

Human Chyle and Lymph. By I. Munk and A. Rosenstein (*Virchow's Archiv*, **123**, 230—279).—In the present research, a female patient, 18 years of age, suffering from elephantiasis of the left leg, was the subject of numerous observations. At varying periods, fistulous communications between the swollen lymphatics and the exterior were spontaneously established, and the lymph which escaped was collected. It was clear under ordinary circumstances, but after a fatty meal was milky, or, in other words, consisted of chyle; this was, no doubt, due to the insufficiency of the valves of the larger lymphatic channels. Previous cases in which it has been possible to collect human chyle or lymph are alluded to; this case seems, however, to be the first in which it has been possible to contrast the properties of the lymph and chyle of the same individual. Observations such as these are also more valuable than those performed on animals, as the period of observation can be more prolonged than in those cases.

The quantities of material available was very large, about 130 grams of chyle being collected per hour during digestion, and about half that quantity of lymph during periods of inanition. By availing themselves of religious fast days, the observers were able to make observations on the fluid collected throughout long periods (18 to 20 hours) of abstinence, and to compare it with that obtained in periods during which various diets were administered.

Hunger-lymph, collected at least 12 hours after a meal, is an almost clear, yellowish fluid, of alkaline reaction, of sp. gr. 1·016 to 1·023, faint odour, and saline taste. On standing, it coagulates, the clot consisting of fibrin and varying numbers of leucocytes.

Red blood-corpuscles and free hæmoglobin were absent on all occasions but one, which occurred during a menstrual period. The lymph-serum contained 94 to 96 per cent. of water, and of the solids, albumin was the most abundant constituent. The following numbers were obtained in two analyses :—

	I.	II.
Total proteïd per cent.	3·516	3·544
Albumin.......	2·818	2·489
Globulin	0·698	1·055
Globulin : albumin	1 : 4	1 : 2·4

The amount of extractive nitrogen was 0·135 per cent. The ethereal extract (fat, lecithin, and cholesterol) was 0·06 to 0·063 per cent. The alkalinity in terms of sodium carbonate was 0·152 to 0·183 per cent. In normal lymph, it is probably higher, as acids are formed during coagulation.

Chyle collected during digestion periods is milky two hours after the meal, and more markedly so three hours after. Fat droplets are scanty, the fat being present in the finest molecular state of subdivision. After a diet containing little fat, the percentage in the chyle is from 2 to 3 per cent. After a fatty meal, it rises to 4 or 5 per cent. The amount of water sinks in a corresponding degree. When the fistula was open, about 60 per cent. of the fat given was recovered in the chyle during the 13 hours following a meal. A comparatively small fraction must therefore have entered the blood stream, or been saponified, or escaped with the fæces. The fact that little entered the blood stream was confirmed by analysis ; during both hunger and digestion, the ethereal extract of the blood was approximately 0·17 per cent., if the fistula was open ; whereas, during fat digestion, when the fistula was closed, the percentage rose to 0·43. From this it was judged that an examination of the chyle at repeated intervals after a meal would give a correct measure of the rate of absorption. Zawilski (*Arbeiten physiol. Anstalt Leipzig*, 1876, 147) stated that in dogs the absorption of fat began two hours, and reached its maximum about 10 hours, after a meal. In the present research, it was judged advisable to make experiments with different varieties of fat.

Olive oil, to which 6·4 per cent. of free oleïc acid was added, was taken as an instance of fluid fat. The chyle was analysed hourly. About 60 per cent. was recovered in 13 hours. Absorption began, as indicated by the rise in the percentage of fat in the chyle, between two and three hours, and reached a maximum from four to six hours, after the meal. The fat separated from the chyle had the characters of the fat in the food, except that it contained only 2·4 per cent. of free oleïc acid. The soaps in the chyle corresponded with about 4 per cent. of the fat given. About one-fourteenth of the ethereal extract consisted of lecithin, and one-fourteenth of cholesterol. The proportion of lecithin : cholesterol : fat = 1 : 1 : 12. Hoppe-Seyler, in a case of chylo-thorax, gives the proportion 1 : 1·6 : 9·6 ; Hasebroek, in a case of chylo-pericardium, as 1 : 1·9 : 6·1 (Abstr., 1888, 736).

Other researches were similarly made with mutton suet ; about 55 per cent. was recovered in the chyle. The maximum was reached in the fifth hour, but the percentage of fat in the chyle remained, high until the eighth hour after the meal, or about two hours longer than in the case of olive oil.

Fatty acids were then given, pure erucic acid being selected. About 45 per cent. of this was recovered in the chyle, not, however, as the free acid, but in the form of the glyceride, erucin; the synthesis probably occurs in the epithelial cells of the intestinal mucous membrane; only a trace of soap was found in the chyle.

Lastly, spermaceti was given; again the chyle had the usual milky appearance. The fat appears to be broken up in the intestine into palmitic acid and cetyl alcohol; the former is absorbed, about 15 per cent. being recoverable in the chyle. It is not, however, absorbed as the free acid, but appears in the chyle as palmitin, the synthesis with glycerol occurring as before in the epithelial cells. This experiment thus furnishes the key to the *modus operandi* of the fact so often previously observed, namely, that animals will lay on normal fat even when fed on spermaceti and other unusual forms of fat. In experiments on dogs, even more spermaceti is absorbed than in man.

W. D. H.

Synthesis of Fatty Acids in the Animal Organism. By WALTHER (*Chem. Centr.*, 1891, i, 189—190; *Centr. Physiol.*, **4**, 590—591).—The author's experiments, the results of which support Munk's views, were made with dogs, some of which were fed on egg albumin and starch, whilst others had fatty acids in addition to this food, and the results showed that the lymph of the former contained very little either of fatty acids or fats, whereas the lymph from the latter contained little fatty acids but much fat, and since the mucous membrane of the stomach did not in any case contain any large amount of fats or fatty acids, whilst, on the other hand, that of the intestinal canal contained very considerable quantities of fat, the author concludes that it is here that the fats are synthetically formed from the fatty acids.

The author also found in the intestinal canal a crystalline substance, soluble in ether, which contains lecithin. The amount of lecithin found in the stomach and canal was too small to account for the glycerol in the fat formed. J. W. L.

Butter Fat. By M. SCHRODT and O. HENZOLD (*Landw. Versuchs-Stat.*, **38**, 349—371).—The object of the experiments was to ascertain the variations in the amount of insoluble and of volatile fatty acids in butter fat, and the relation of these variations to the period of lactation and to the feeding. The experiments, which extended over a year, were made with 10 cows (3 varieties). The winter feeding was meadow hay (6 to 7·5 kilos.), oat-straw (1·5 to 2·5 kilos.), beetroot (5 kilos.), wheat bran (3 to 4·5 kilos.), cotton cake (1 to 1·5 kilos.), and salt (20 grams). The cream was removed from the milk after 24 hours. The filtered butter fat was kept in well-closed bottles, and several samples examined together. Besides estimating the volatile and insoluble acids, the behaviour towards iodine and the refractive-exponents were observed. The volatile fatty acids were determined in 5 grams of fat by Wollny's method, and the insoluble fatty acids by Hehner's method (also in 5 grams). The amount of acid found is expressed in c.c. of decinormal alkali; the "iodine numbers" are grams of iodine capable of being absorbed by 100 grams of fat. With regard to the volatile fatty acids, the results confirm those obtained by Nilson (*Bied. Centr.*, **18**, 171); the amount depends on the period of lactation and not on the feeding. The amount of oleïn also depends on the period of lactation. The refractive exponent is a fairly constant number. Leaving out of account the four days subsequent to calving, the numbers vary as follows: volatile fatty acids, 21·70 to 34·33; iodine number, 27·38 to 43·46; refractive exponent, 1·458 to 1·463. The results are given in tables. The amount of volatile fatty acids is greatest about two months after calving, after which it decreases as the period of lactation progresses. The amount of oleïn, on the other hand, increases; and the amount of insoluble fatty acids is higher in late than in early periods of lactation. (Compare Mayer, Abstr., 1889, 173, and Vieth, this vol., p. 507).

N. H. M.

Influence of Alkalis on the Glycogen of the Liver. By E. Dufourt (*Chem. Centr.*, 1891, 188—189; from *Centr. Physiol.*, **4**, 589—590).—The author has made seven parallel experiments, six with dogs, and one with a guinea-pig, on the action of sodium hydrogen carbonate on the amount of glycogen formed in the liver. The dogs were allowed to fast for four days, then fed with meat for 8—15 days, the amount being the same for each pair of dogs, and to one of each pair 2—5 grams of sodium hydrogen carbonate per day was given in addition. The dogs were then killed, and the amount of glycogen determined from the difference between the amounts of sugar present as such and that obtained after heating with hydrochloric acid. The following table gives the results:—

	Dog 1.		Dog 2.		Dog 3.		Dog 4.		Dog 5.		Dog 6.	
	No alk.	With alk.	No alk.	With alk.	No alk.	With alk.	No alk.	With alk.	No alk.	With alk.	No alk.	With alk.
Weight in kilograms ..	7·55	9·87	8·5	7·0	8·5	8·0	6·0	6·0	6·8	6·5	9·5	8·2
Weight of liver in grams ...	300	383	215	189	148	190	192	229	271	250	230	190
Sugar........	1·64	3·06	1·5	2·52	1·35	2·43	2·49	3·01	1·62	2·16	2·93	2·56
Glycogen	1·39	5·18	1·5	1·60	0·62	2·28	0·15	3·78	0·09	2·33	0·36	1·43
Total sugar .	2·88	7·91	2·85	4·30	1·83	4·23	2·39	6·49	2·47	4·12	2·99	4·06
Total sugar per 100 of liver.	0·96	2·06	1·32	2·27	1·23	2·22	1·24	2·83	0·91	1·64	1·30	—

The experiment with guinea-pigs was carried out on similar lines, and the result was an increase in the amount of glycogen formed in the liver in every instance.

J. W. L.

Urea. By K. A. H. Mörner and J. Sjöquist (*Skandinav. Archiv Physiol.*, **2**, 438—487).—In view of Schröder's hypothesis (*Arch. exp.*

Path. u. Pharm., **15**, 364) that the liver cells form urea from ammonium salts, it was judged necessary to examine the amounts of urea and ammonia excreted in various liver diseases. In cases of cirrhosis, syphilis, and cancer of the liver there was an increased amount of ammonia, and lessened amount of urea found. The amount of extractive nitrogen was in some cases markedly increased, in others not. Also in cases where no liver disease was present, an increase of ammonia in the urine was sometimes noted; for instance, in a case of fatty heart, one of pyopneumothorax, and especially in a case of tetanus. In a case of ascites and pleurisy, the amount of extractive nitrogen was not increased, and the amount of ammonia was less than normal.

The various methods at present in vogue for the estimation of urea are discussed, and the following new one, ultimately adopted in carrying out the investigation :—

5 c.c. of urine is mixed in a flask with 5 c.c. of a saturated barium chloride solution, to which 5 per cent. of barium hydroxide has been added. To this was added 100 c.c. of a mixture of two parts of 97 per cent. alcohol, and one part of ether, and the whole allowed to remain in a closed flask until the next day. The precipitate is then filtered off and washed with the alcohol and ether mixture. The alcohol and ether are then distilled off from the filtrate (*plus* washings) at 55°. When the volume of the fluid reaches 25 c.c., a little water and magnesia are added, and the distillation continued until the steam has no longer an alkaline reaction, and the volume of the fluid is 10—15 c.c. Some drops of concentrated sulphuric acid are then added, and the whole placed in a flask on the water-bath. The nitrogen is estimated by Kjeldahl's method, and the amount of urea calculated from the nitrogen found. W. D. H.

Schreiner's Base (Spermine). By A. Jürgens (*Chem. Centr.*, 1891, i, 193—194; from *Pharm. Zeit. Russ.*, **29**, 726—732).—Owing to the uncertainty as to the identity of Pöhl's specimen of this base with that of Schreiner, the author has examined both specimens.

From the genital organs of the steer the author has isolated about 0 0003 per cent. of Schreiner's base, and his results substantiate Schreiner's. He considers that the characteristic odour of semen obtained from the aurochloride of the base after treatment with magnesium has only a negative value, since the mother liquors, from which the phosphate of the base had been separated, gave the same smell after like treatment.

From the spermine, after treatment with magnesium, a derivative is obtained which is also present in the testicles, and which must, therefore, be already formed in the semen. Pöhl's specimens, prepared during May, June, July, and August, contained no spermine. Ammonium phosphate and ammonia produced no crystalline precipitate, auric chloride precipitated an amorphous substance, platinic chloride gave cubical and not prismatic crystals. Calculated on the dry substance, the author found 54 per cent. of mineral matter and 43 per cent. of sodium chloride in a July specimen, in an August specimen 59·35 per cent. of mineral matter and 56·8 per cent. of salt, whilst the dry substance contained in the "2 per cent." solutions amounted to 2·2 and 2·1 per cent. respectively, so that of the so-called spermine only about 1 per cent. was present. The biuret reaction for peptone was positive. J. W. L.

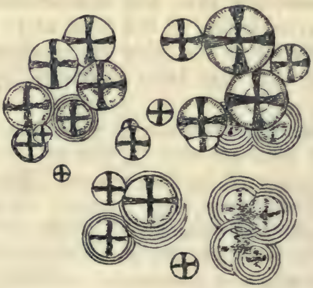
Diastatic Ferment in Urine. By ROSENBERG (*Chem. Centr.*, 1891, i, 185; from *Centr. Physiol.*, **4**, 587—588).—The author found varying quantities of a diastatic ferment in human urine, the greatest quantities occurring a few hours after taking food. The ferment was detected both directly and indirectly after extraction with fibrin, by adding a little starch paste at the body temperature, and then testing for sugar with 5 per cent. potash or by Trömmer's test.

Experiments with animals showed that ligaturing the ductus Stenoniani only increased the diastatic ferment in the case of herbivoræ, not with the carnivoræ, which only show traces of the ferment in the urine.

Trypsin and fat ferment were never detected in fresh human urine or in that of carnivoræ; in rabbits only when the ductus Wirsungianus was ligatured; with herbivoræ, after this procedure the diastatic ferment appeared in the urine. J. W. L.

Artificial Preparation of Sphæroliths of Uric Acid Salts. By W. EBSTEIN and A. NICOLAIER (*Virchow's Archiv*, **123**, 373—376). —If some uric acid be dissolved on a microscope slide in a dilute alkaline solution, and watched with the microscope, there is, after slight concentration, a formation of round particles of urates varying in diameter from 2 to 100 μ. These are mixed with needles, either singly or in bundles. As solvents, sodium hydroxide, potassium hydroxide, lithium carbonate, borax, ammonia, and piperazine were used; the best results were obtained by using the uric acid sediment from human urine.

With the polarising microscope between crossed Nicols, the sphæroliths showed a right-angled, black interference cross, the arms of which lay parallel to the polarisation planes of the Nicols, and, concentric with the middle point of this cross, coloured interference rings were seen.



Similar sphæroliths were obtained with sodium hydrogen carbonate, so that they may consist either of acid or normal urates.

The interest of such an observation as bearing on the formation of urinary calculi is pointed out. W. D. H.

Pathology of Proteïds. By S. Martin (*Brit. Med. J.*, **1**, 1891, 159—161).—The changes in structure that occur in a diseased tissue or organ are associated with chemical changes, and it is to certain changes in the proteïds, the most abundant constituent of most living structures, that attention was chiefly directed in the present research.

Although peptones and albumoses are formed in the alimentary canal, their presence elsewhere in the body is pathological, as during normal absorption they are regenerated into the blood proteïds. The action of micro-organisms during putrefaction is, first, similar to that of pepsin, namely, it forms albumoses and peptones, but, subsequently, ptomaïnes may make their appearance. Putrefaction (using the word in the wide sense of the changes due to microbes) is, moreover, a frequent factor in pathological processes, and albumoses and peptones are poisonous substances. If these poisons are formed in decomposing collections of cells, as in abscesses, empyema, phthisis, &c., they pass into the lymph and blood-stream, passing ultimately from the body by the urine, constituting what is generally termed peptonuria, but which should be more properly called albumosuria, the proteïd which is present being deutero-albumose. Illustrative cases are quoted which show the amount of albumose in the pus and in the urine before and after the evacuation of the abscess, the albumose in the urine varying with the amount of accumulated pus.

One of the most striking features of pus-formation which is common to it and albumose poisoning is fever. It is possible that other factors have also to be considered; thus leucine, often found in pus, is a fever producer; alkaloïds, if they do exist, have yet to be isolated.

In ordinary pus, the agent which forms the albumoses is probably not an enzyme, but the *Staphylococcus pyogenes aureus;* in tubercle, it may be the tubercle bacillus.

But the presence of albumoses in disease cannot always be ascribed to micro-organisms, as in glycosuria and osteomalacia. In osteomalacia the diseased bones contain an albumose similar to that excreted in the urine, and perhaps due to the rapid breaking down of lowly-organised cells. In the puerperal state, the origin of the albumose may be the degenerating cells of the hypertrophied uterus which is undergoing involution. The origin of albumoses in other cases, such as measles, is at present involved in obscurity. W. D. H.

Specific Gravity of Blood in Disease. By S. M. Copeman (*Brit. Med. J.*, **1**, 1891, 161—163).—The method used differs from that of Roy (Abstr., 1887, 608), by the fact that the standard solutions of glycerol and water used contained considerable quantities of boroglyceride and magnesium sulphate, and a small amount of corrosive sublimate. These solutions keep perfectly.

A number of observations on the specific gravity of the blood, in cases of disease chiefly of an anæmic character, are recorded. It was found that when a rise of density of the blood is produced artificially, as by a ligature round a limb, it is accompanied by a corresponding rise in corpuscular richness; and in cases of disease also, it appears that the number of corpuscles is an important factor, if not the most important. But in some cases, the specific gravity of the plasma must vary also, particularly in one case of pernicious anæmia, in which the specific gravity of the entire blood was only as high as that of normal plasma. W. D. H.

Idiosyncrasy of certain Animals with respect to Phenol. By Zwaardemaker (*Compt. rend.*, **112**, 492—493).—Quantities of phenol insufficient to produce any evil effects on dogs and rabbits, throw cats and rats into violent convulsions, terminating in death from respiratory paralysis. As little as 11 milligrams per kilo. of body weight was sufficient to produce slight convulsions in an adult cat. This idiosyncrasy is probably due to a peculiar excitability of the nervous centres. C. H. B.

Physiological Action of Thebaïne, Narcotine, and their Derivatives. By R. Stockman and D. B. Dott (*Brit. Med. J.*, **1**, 1891, 157—159).—In continuation of a previous research (Abstr., 1890, 1178), certain opium alkaloïds and some of their derivatives were studied, and the results confirm the conclusion previously arrived at, that the addition or substitution of certain radicles modifies very superficially the original action of the alkaloïd.

Thebaïne (vinyl ether of morphine, $C_{17}H_{18}(C_2H_3O)NO_2$, Grimaux) in physiological action belongs to the morphine group. It stands, however, at its extreme limit, and more closely resembles strychnine than morphine; a slight preliminary narcotic stage, observed after small doses, stamps it, however, as somewhat different from strychnine.

Methylthebaïnium sulphate, $(C_{19}H_{21}NO_3CH_3)_2SO_4$, is obtained by adding methyl iodide (1 mol.) to thebaïne, and decomposing the iodide formed with silver sulphate. Its crystals are colourless, and freely soluble in water. From experiments on frogs and rabbits, the conclusion is drawn that the physiological action of the drug is not very different from that of thebaïne; its tetanising power is, however, diminished, and its paralysing action on cord and motor nerve terminations is increased.

Narcotine, $C_{22}H_{23}NO_7$, *cotarnine*, $C_{12}H_{13}NO_3$, and *hydrocotarnine*, $C_{12}H_{15}NO_3$, were also examined. These also all belong physiologically to the morphine group, their chemical differences altering their action in degree but not in kind. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Cultivation Products of the Tubercle Bacillus. By E. M. Crookshank and E. F. Herroun (*Brit. Med. J.*, **1**, 1891, 401—403).—In cultivations of the tubercle bacillus in glycerol broth, albuminous substances of the nature of albumose and peptone were identified, and also a substance which gives the reactions of an alkaloïd. The latter was, however, obtained in too small a quantity for more than a qualitative analysis. Injected into animals, symptoms similar to those produced by Koch's "tuberculin" were obtained.

W. D. H.

Bacterial Decomposition of Cane-sugar with Formation of a New Lactic Acid. By F. SCHARDINGER (*Monatsh.*, **11**, 545—559). —See this vol., p. 666.

Conversion of Starch into Dextrin by the Butyric Ferment. By A. VILLIERS (*Compt. rend.*, **112**, 435—457).—See this vol., p. 659.

Formation and Migration of Carbohydrates in Leaves. By W. SAPOSCHNIKOFF (*Chem. Centr.*, 1891, i, 93—94; from *Ber. deut. bot. Gess.*, **8**, 233—242).—1. *The Migration of the Carbohydrates out of the Leaves.*—The results of the author's experiments show that the carbohydrates pass out of the leaves much more quickly when on the plant, than when cut off and laid in water; that they pass from the leaves the more quickly, the fewer the number of leaves; and that this rate depends on the rapidity of growth. In spring and summer all the starch disappears in 1—2 days or less, whilst in winter the process occupies from 7—14 days. The starch is probably transformed into glucose previous to passing out of the leaf, and the rate at which this change takes place depends on the rate at which the soluble product, glucose, passes away. The starch contained in leaves cut off and placed in water remains for a week or more unchanged, whilst that in leaves on the plant frequently disappears in 12 hours.

2. *Formation of Carbohydrates.*—In order to determine the rate of formation of carbohydrates in the leaves, the amount actually present was determined, and the rate of migration was allowed for. The following figures, expressing the weight of carbohydrates in grams formed per square metre of leaf per hour, were obtained in this way for the varying states of the weather.

Plant—*Helianthus annuus*, sky-clear = 0·729 and 0·481; clear, but a few clouds = 0·594 and 0·428; clear, with frequent white clouds = 0·379; beclouded = 0·140, 0·147, and 0·141. For *Cucurbita pepo*, the following were found: clear sky = 0·403, and cloudy = 0·298, showing a more rapid formation under a clear sky.

In the case of leaves cut off the plant, the amount of carbonic anhydride assimilated is limited, probably owing to the collection of assimilated substance. A leaf, containing no starch, and which had been kept for two or three days in darkness, was better able to assimilate carbonic anhydride than one which had not been kept from the daylight, but which contained starch. From experiments on the assimilation of carbonic anhydride, it was found that there was not so much glucose formed in the leaf as corresponded with the amount of carbon absorbed, and the author concludes that some other substance is formed besides glucose.

J. W. L.

Assimilation of Nitrogen from the Air by Robinia pseudacacia. By B. FRANK (*Chem. Centr.*, 1891, i, 93; from *Ber. deut. bot. Gess.*, **8**, 292—294).—One seed of *Robinia pseudacacia* was allowed to germinate in each of a series of pots containing sterilised, nitrogen-free quartz sand, mixed with a non-nitrogenous nutrient solution. To the sand was added a small quantity of earth, taken from where old *Robinia* were growing. The germination and growth proceeded normally, and at the end of 125 days the plants were 22 cm. high, and had from 5—7 leaves each, which measured from 9—18 cm. in length. On the roots of each plant, a number of nodules had formed. varying in size from that of mustard seeds to that of a pea. Some of these were entirely empty, whilst others had commenced to undergo this process. The dry substance of four of the plants weighed 4·411 grams, and contained 0·092 gram of nitrogen; the nitrogen contained in the seeds of these plants amounted to 0·0024 gram.

J. W. L.

Analysis of Milk of Ripe and Unripe Cocoanuts. By L. L. VAN SLYKE (*Amer. Chem. J.*, **13**, 130—131).—The milk of the unripe nuts was transparent like water, containing in suspension a little cloudy-white substance, which was readily removed by filtration. In the ripe nut, the milk was quite turbid in appearance, and did not filter clear. The specific gravity was determined by a picnometer, water by drying at 60°, and proteïds by Gunning's modification of Kjeldahl's method. Hammerbacher's analysis probably refers to ripe cocoanuts.

	Milk of unripe cocoanuts.						Milk of ripe cocoanut.	Hammerbacher's analysis.
	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.
Weight in grams......	230·5	378·6	347·0	383·7	350·0	330·0	109·6	151·9
Sp. gr. at 15·5°.......	1·0246	1·0230	1·0223	1·0230	1·0221	1·0215	1·0440	1·0412
Water, per cent., at 60°	94·37	94·48	94·59	94·89	95·27	96·43	91·23	91·50
Ash, per cent.........	0·575	0·635	0·675	0·611	0·608	0·602	1·06	1·19
Glucose, per cent.	4·58	3·83	3·45	4·06	4·36	3·56	trace	—
Cane sugar, per cent. ..	trace	trace	trace	trace	trace	trace	4·42	—
Proteïds, per cent.	0·120	0·126	0·114	0·205	0·140	0·095	0·291	0·46
Fat per cent. (ether extract)	0·084	0·100	0·138	0·131	0·145	0·120	0·145	0·07

A. G. B.

Analyses of Beetroot Seed. By N. LASKOWSKY (*Landw. Versuchs-Stat.*, **38**, 317—319).—The analysis of the seeds gave the following results:—Water, 10 per cent.; proteïds, 20·13; fat, 17·05; crude fibre, 4·54; ash, 3·74; cellulose free from nitrogen, 44·54. Various samples were examined with regard to the quantity of fat contained in the seed; the percentages found varied from 23·09—20·76.

E. W. P.

Composition of Drainage Waters. By P. P. Dehérain (*Compt. rend.*, **112**, 465—469).—Experiments were made with soils from different parts of France, two from the north and two from the district of Limagne, in the Auvergne. The experimental pots contained 50 kilos., and the results are calculated to kilos. per hectare; from March to December, 1890, the quantity of nitric nitrogen lost in the drainage waters was as follows:—

Soil from—	
Wardrecques (Pas de Calais)	152·4
Blaringhem (Nord)	128·1
Marmilhat (Puy de Dome)	62·5
Palbost (Puy de Dome)	45·2

The soils from the north lose a much greater quantity of nitrates, although they are poorer in nitrogen than the soils of Limagne. No definite relation could be traced between the quantity of nitrates formed in the soil and the quantity of water retained. The smaller quantity of nitrates in the soils of Limagne is probably due to the fact that they contain a large quantity of organic matter, which, as Warington and Winogradski have shown, retards nitrification. The two soils from the north lose their fertility rapidly, owing to the great loss of nitrates in the drainage, and they require constant manuring, whilst the soils of Limagne require much less constant attention.

The quantity of nitrates in soils is usually deficient in spring, but nitrification proceeds rapidly in the autumn, and after harvest there is often great loss of nitrogen in the drainage. During October, 1889, soils at Grignon lost 72·2 kilos. of nitric nitrogen per hectare. The author has previously proposed to sow, after harvest, some rapidly growing plant, such as mustard, rape, or colza, in the hope that these crops would retain the nitrates, and when worked into the soil in the late autumn, or in spring, would restore to the soil the nitrogen which would otherwise have been lost in the drainage, besides providing a useful organic manure. Experiments in this direction were made in the autumn of 1890, and, although the season was unfavourable, the results were satisfactory. From July to November there was very little rain, and the consequent dryness of the soil retarded nitrification, so that the loss in the drainage of bare soils was much below normal. From November 1st to 7th, 1890, the loss of nitric nitrogen in kilos. per hectare from bare soils was as follows:—

Beet-root gathered in October	7·5
Maize gathered in August	14·5
Hemp gathered in August	10·5

With a protective crop, the loss during the same period was very small indeed.

Colza, after oats	0·37
Rape, after peas	0 51

If the protective crop is killed by frost before it has been worked into the soil, its efficiency disappears. Colza, however, will live through the winter in comparatively mild climates, and in severe climates, since the loss by drainage during December is always very small, the crop may be worked into the ground in November.

Whether the nitrogen retained will repay for the cost of seed and of labour depends on circumstances, and especially on the actual value of the loss by drainage. It seems to be better to use *Leguminosæ* with *Cruciferæ* for the protective crop, instead of *Cruciferæ* alone, but the author will report subsequently on experiments in this direction. C. H. B.

Analytical Chemistry.

Reactions for Microchemical Mineral Analysis. By H. Behrens (*Jahrb. f. Min.*, Beilage **7**, 434—470).—By the investigations of Haushofer and of Streng the employment of the microscope in chemical investigations has been greatly extended. The method was originally confined to the identification of the rock-forming minerals. At the present time, it forms a valuable aid to qualitative analysis. The saving of time, of material, and of working space presents such great advantages for the microchemical method, that anyone who has had practice with this method would invariably use the microscope for certain reactions, such as for potassium, calcium, and magnesium. The author has, therefore, prepared this paper, which is too lengthy to admit of complete abstraction, giving complete instructions for conducting microchemical mineral analyses. After giving details as to the mode of dissolving the material to be examined, he deals with decantation and filtration, sublimation, evaporation, instruments, and reagents, and finally devotes 28 pages to an enumeration of the microchemical reactions of the various elements, arranged in alphabetical order. B. H. B.

Apparatus for the Estimation of Water in Mineral Analysis. By T. M. Chatard (*Amer. Chem. J.*, **13**, 110—113).—Many minerals lose the whole of their water only when heated for a considerable time at a temperature at which glass softens; for such, the author employs a platinum tube. A figure in the original paper represents a convenient form of tube, and an air-bath specially adapted for the preliminary drying before the ignition. The tube is 250—300 mm. long, and 16 mm. external diameter; it tapers at one end into a tube 80 mm. long and 5 mm. diameter, to which is sealed a glass adaptor, for connection with the absorption apparatus. The other end of the larger tube is fitted with a collar of phosphor-bronze, into which fits a perforated stopper of the same metal. That portion of the tube which is to be heated, is rendered impervious to the gases of the flame, and at the same time protected from injury, by a wrapping of asbestos-paper soaked with a saturated solution of borax; this is in its turn covered with a sheet of platinum foil, and then highly heated and slowly cooled. The platinum boat containing the substance is placed in a cylinder of platinum foil, closed at the end nearest the stopper by a cap, in which there is a small hole to allow of the passage of the air current; this cylinder, whose object is the prevention of loss by spurting, is thrust into the coated portion of the large tube, together with two rolls of platinum gauze, one at each end of the cylinder. A. G. B.

Detection and Estimation of Hydrochloric Acid in Gastric Juice. By A. Fawizky (*Virchow's Archiv*, **123**, 292—309).—Hydrochloric acid is usually detected in the gastric juice by means of certain colour reactions. It is well known that proteïds form, with hydrochloric acid, loose combinations, and the presence of these substances may, therefore, interfere with tests for the acid. These substances, or their digestive products, conveniently grouped under the heading peptone, are apt to occur in the stomach; hence the necessity of ascertaining correctly the value of these colour reactions in their presence. Ewald (*Zeit. Klin. Med.*, **1**, 619) pointed out that the presence of peptone interferes with the methyl-violet and tropæolin reactions. Seemann (*ibid.*, **5**) made some qualitative experiments in the same direction; and Moritz (*Deutsch. Arch. Klin. Med.*, **13**), from observations on two healthy persons, found that the reactions with congo-paper and tropæolin did not succeed when the proportion of peptone to acid exceeded 8 or 12 to 1. In the present research, attention was particularly directed to the most delicate of these colour tests, namely, the methyl-violet reaction, and Günsburg's phloroglucinol reaction, with the result, similar to that obtained by Moritz, that the reactions did not succeed when the proportion 9 : 1 was exceeded.

The acidity of gastric juice may be due to hydrochloric acid, lactic acid, and fatty acids; and the question next investigated was whether an approximate estimation of the hydrochloric acid might be made by simply titrating with standard alkali, supposing that lactic acid, as tested for by Uffelmann's reaction, was absent; it was found that such a simple method gives fallacious results.

The best method is considered to be that of Sjöquist (Abstr., 1889, 302); the end reaction is, however, rather obscure, and several modifications have consequently been suggested. Thus, v. Jaksch (*Sitzungsb. Wien. Akad.*, **98**, Abth. 3, 1890) estimates the barium chloride, gravimetrically, as the sulphate. Salkowski suggested to the author a modification which would not be so lengthy as this, and a series of experiments on artificial mixtures of hydrochloric and lactic acids, and peptone shows that it is equally delicate. The method consists in adding excess of barium carbonate to 10 c.c. of the test liquid, evaporating to dryness, and burning off the organic residue. The barium chloride is extracted with hot water, filtered, and sodium or ammonium carbonate added to the filtrate, until the barium is completely precipitated as carbonate. The precipitate is collected, washed with water until the washings give no reaction with silver nitrate; it is then dissolved in hydrochloric acid, evaporated to dryness, dissolved in water, and the chlorine titrated with a standard silver nitrate solution, with potassium chromate as indicator. The solubility of barium carbonate in water is so slight as to make no practical difference in the result.

Bourget's modification (*Arch. Med. exper. Anat. Pathol.*, p. 444) is very similar. He dissolves the barium carbonate in a known quantity of hydrochloric acid, and then titrates with normal soda.

W. D. H.

Mode of Combination of Sulphuric Acid in Plastered Wines, and the Detection of Free Acid in Wines. By L. Magnier de la Source (*Compt. rend.*, **112**, 341—343).—The author criticises the paper of Roos and Thomas, and considers that when a wine has been thoroughly plastered, some of the potassium must necessarily be present as hydrogen sulphate when a formation of potassium hydrogen tartrate has taken place.

Sulphuric acid added to wine in quantity exceeding 1 gram per litre cannot be detected in the ash, unless potassium carbonate is added before evaporation. This is the limit at which the presence of the acid can be distinctly recognised by the taste. C. H. B.

Separation of Titanium, Chromium, Aluminium, Iron, Barium, and Phosphoric Acid in Rock Analysis. By T. M. Chatard (*Amer. Chem. J.*, **13**, 106—110).—The author asserts that success with this process, which is a combination of several methods, depends on careful attention to numerous details, for which the original must be consulted. The following gives an outline of the process. Silica is eliminated by evaporation with sulphuric and hydrofluoric acids. The residue is treated with hydrochloric acid, which leaves barium sulphate and unattacked minerals; fusion with sodium carbonate decomposes the latter, and enables the barium to be determined. The original hydrochloric acid solution and the various secondary solutions obtained during the fusion and the precipitation of the barium, all of which should contain the chromium and iron as sesquioxides, are mixed, precipitated with ammonia, the precipitate redissolved, and again precipitated to eliminate magnesium. The precipitate is once more dissolved, the solution evaporated, and the residue fused with sodium carbonate and nitrate. The melt is dissolved in water, and the titanium determined in the insoluble portion by Gooch's method (*Proc. Amer. Acad.*, **12**, 435; Abstr., 1886, 492). The solution containing chromic and phosphoric acids is heated with ammonium nitrate as long as aluminium phosphate and hydroxide are precipitated; the phosphoric acid is determined by the molybdate method. The filtrate is precipitated with ammonia and ammonium sulphide; the precipitate is dissolved, the solution oxidised, evaporated, treated with sodium hydrogen carbonate, and filtered after some hours; this eliminates any remaining alumina, after which the chromium is reduced, and precipitated with ammonium sulphide.

A. G. B.

Quantitative Estimation of Pentaglucoses (Pentoses) in Vegetables. By G. de Chalmot and B. Tollens (*Ber.*, **24**, 694—695).—The authors have improved the method of Günther and

Tollens (Abstr., 1890, 1352). The decomposition of the substances is effected as before, with hydrochloric acid, but the furfuraldehyde, instead of being titrated, is precipitated with phenylhydrazine acetate, and the hydrazone weighed. The distillation is conducted on a bath of Rose's metal, with hydrochloric acid of sp. gr. 1·06 (100 c.c.), fresh portions of the latter being added until the distillate no longer gives the furfuraldehyde reaction. It is then made faintly acid with acetic acid, and in a determinate volume, precipitated with phenylhydrazine acetate, the hydrazone being collected in an asbestos filtering tube, dried in a special drying apparatus in a vacuum at 50—60° and weighed; a correction is applied for its solubility.

Arabinose, when small quantities (0·2 gram) are taken, yields 52·7 per cent., and with larger quantities (0·5 gram), 47·7—50·2 per cent.; and xylose, 56—59 per cent. of furfuraldehyde. The mean yield is: Arabinose, 48·72 per cent.; xylose, 56·25 per cent.; and pentaglucoses (pentoses), generally 52·5 per cent. of furfuraldehyde.

Quantitative estimations of pentaglucoses (pentoses) in the undermentioned substances (of which 2—5 grams were taken), by this method gave the following results:—

Cherry gum........	45—46	per cent.	Arabinose.
Wheat-straw	24·9	,,	xylose.
Oat-straw..........	22·6	,,	,,
Beech-wood........	19·7	,,	,,
Fir-wood	7·8	,,	,,

Duplicate estimations of the above gave a maximum difference of 0·6 per cent. of furfuraldehyde. It is thus established that pentaglucoses (pentoses) are very widely distributed in nature.

A. R. L.

Estimation of Invert-sugar in Molasses. By STRIEGLER (*Chem. Centr.*, 1891, i, 211—212; from *Zeit. Vereins Rübenzückerind.*, 1890, 418, 964—975).—The author prefers Soldaini's reagent to that of Nessler for the determination of the invert-sugar in molasses, and he also prefers clearing with sodium carbonate and "blood-charcoal" to lead acetate. He recommends the following method:—10 grams of molasses is weighed and dissolved in a 100 c c. flask with 70 c.c. of water, precipitated with sodium carbonate, and warmed at 90—95°, until the precipitate becomes dense, then cooled by immersion in cold water, diluted to 100 c.c., and shaken with 1—2 grams of blood-charcoal. 50 c.c. of the filtrate is added to 100 c.c. of Soldaini's reagent, which must be in a state of ebullition; the liquid is heated further until boiling again commences, boiled for four minutes, and allowed to rest for one minute. It is then filtered through a double filter, and after one-half or two-thirds of the filtrate has passed through, it is returned to the filter again, after which the precipitated cuprous oxide is washed with potassium hydrogen carbonate solution, until free from cupric sulphate, and then finally washed with hot water.

From the author's results, 50 milligrams of invert-sugar reduce from 140·5 to 144·5 milligrams of copper; Herzfeld found 133 8 milligrams; Bodenbender and Scheller found 141—142 milligrams.

J. W. L.

Estimation of Free Fatty Acids in Fodder. By G. Loges and C. Claessen (*Landw. Versuchs-Stat.*, **38**, 314—316).—Four methods of estimating the free fatty acid in fodders were compared for accuracy. The methods were:—(1) to extract with ether, and titrate after previous drying for three hours; (2) after three hours' drying, to add alcohol to the ethereal extract, and then titrate; (3) without previous drying, to extract and treat as in (2); (4) to digest for three hours in cold ether, and titrate aliquot portions of the filtrate, with addition of alcohol; an alcoholic solution of sodium hydroxide was employed, and phenolphthaleïn used as indicator. Results:—(1) gives too low values, as in estimating the fat of many fodders a loss occurs by volatilisation during drying, and also the drying of the ethereal extract results in loss by volatilisation. Methods (3) and (4) yield results which agree well together, and these two methods are the only ones which can be recommended to produce trustworthy results.

E. W. P.

Alterability of some Food-fats. By O. Reitmair (*Landw. Versuchs.-Stat.*, **38**, 373—400).—The acidity, behaviour towards iodine, and the behaviour when saponified, of several fats was investigated. The following are the most important results:—Earth-nut fat is very changeable. When fresh it is nearly clear and thin, with a slight and agreeable taste and odour; it contains no free fatty acids, and its saponification number is the least, and the iodine number the highest, of any observed.

The expressed earth-nut oil changes slowly; only when much exposed to light it becomes, after a long time, viscous and rancid, and has then a lower iodine number and a higher saponification number.

The fat in earth nuts changes slightly when the outer shells remain uninjured. The fat of earth-nut cake changes most, and especially when the cake is poor in fat. The "acid number" of the fat rises quickly after the pressing out. The iodine number may sink to one-third of its original value, especially in the case of old and bad nuts.

To judge of the freshness of earth-nut cake from the character of the fat, the appearance of the fat is the first thing to be considered. If solid at the ordinary temperature, much free fatty acid is present, and the less there is of fatty acid the softer the fat will be. The high iodine number of the fat is the best criterion for the freshness of the cake, and of the seed from which it was prepared.

N. H. M.

Detection of Tannin in Plants. By T. Waage (*Chem. Centr.*, 1890, ii, 1030; from *Apoth. Zeit.*, **5**, 685—686).—The author considers a solution of perfectly anhydrous ferric chloride in ether to be the best reagent for tannin in plants, since the aqueous solution reacts with other substances besides tannin. Iodine and zinc chloride has the objection that it reacts with gallic acid. Potassium dichromate is a very delicate reagent, but reacts also with hydroxy-aromatic substances. The author discusses the values of the reagents recommended by Loew and Bokorny, Gardiner, Darwin, Moll, and Klercker. Pfeffer's reaction, the fixing of aniline dyes, applies not only to tannin, but to phloroglucinol also. J. W. L.

Estimation of Urea. By K. A. H. Mörner and J. Sjöquist (*Skandinav. Arch. Physiol.*, **2**, 438—487).—See this vol., p. 758.

Determination of Nicotine in Presence of Ammonia. By A. Pezzolato (*Gazzetta*, **20**, 780—798).—The method proposed by the author is based on the neutral reaction of a solution of nicotine in 96° alcohol to litmus and alizarin, and on the insolubility of normal ammonium sulphate in alcohol of the same strength. The substances containing the nicotine and ammonia must be distilled in a current of steam with some alkali, which does not decompose nicotine, and the distillate collected in a known volume of normal sulphuric acid sufficiently large to yield the acid salts of the base. The best alkali for distilling with the materials from which the nicotine is to be separated is magnesia, as this has no action on either nicotine or the associated proteïd matters. The distillate is then reduced by evaporation to a volume of 50—100 c.c., coloured with a drop of litmus or alizarin, titrated with a decinormal or normal solution of potash or soda, and evaporated to dryness on the water-bath; the residue, which consists of the sulphates of nicotine, ammonium, and potassium or sodium, is taken up with 60 c.c. of alcohol (98—99°), which dissolves only the nicotine sulphate. The solution is titrated in presence of the insoluble salts with an alcoholic decinormal solution of potash or ammonia (prepared by mixing 100 c.c. of a normal aqueous solution with 900 c.c. of absolute alcohol), finishing as soon as the suspended salts become slightly coloured. For every 30 c.c. of the decinormal solution used, an addition of 20 c.c. of 98—99 per cent. alcohol must be made to maintain the alcoholic strength of the solution. The partial dissociation (1·3 per cent.) of the ammonium sulphate, on evaporating to dryness, renders a slight correction necessary. The amount of acid found to represent the ammonia present must be multiplied by 1·013 to obtain the real figures, and the difference must be subtracted from the quantity of acid representing the nicotine. The necessity for making this correction may be avoided by re-acidifying the sulphuric acid solution after titration, and before evaporating to dryness, and adding to the dry residue a quantity of alkali corresponding exactly with the amount of acid added; taking care that the strength of the alcoholic solution titrated does not fall below 96—97°.

A large number of experiments are given to prove the accuracy of the above methods. S. B. A. A.

Estimation of Morphine. By G. Looff (*Chem. Centr.*, 1890, ii, 1034; compare Abstr., 1890, 1349, and Dietrich, this vol., p. 511).—Replying to Dietrich's criticisms on his method, the author contends that the employment of potassium carbonate has its advantages;

that since he has found calcium sulphate in morphine extracts, the precipitation as oxalate is not unnecessary; that a concentrated extract of opium contains a larger quantity of colouring matter than a dilute one: and that it is better to evaporate the ether layer, because morphine has been found in it after ten minutes' shaking.

J. W. L.

The Assay of Quinine Sulphate by the Ammonia Process. By L. Prunier (*J. Pharm.* [5], **23**, 163—170).—After an examination of the whole process, the following procedure is recommended. The sulphate is dried at 100°, and an amount is weighed off equivalent to 2 grams of the original sample, agitated with 35 parts of water (calculated on the anhydrous salt) boiled for one or two minutes to complete solution, and, after replacing the water boiled off, the solution is allowed to cool to 15°, and filtered at that temperature. 5 c.c. of the filtrate is measured into each of three flasks, and ammonia of 0·96 sp. gr. is run steadily in to the first one until a slight precipitate remains undissolved; this, for example, may take 7·5 c.c. The second flask, with 8 c.c., may yield a slight opalescence. Finally, the third receives 8·5 c.c., and gives a transparent liquid; if this remains transparent for about a quarter of an hour, the assay indicates 8·5 c.c. But if the second flask becomes clear after some minutes, and remains limpid, then 8 c.c. is the definite result.

J. T.

Toxicological Observations. By F. Ciotto and P. Spica (*Gazzetta*, **20**, 619—631).—After pointing out the indecisive character of the tests hitherto proposed for vegetable alkaloïds in presence of ptomaïnes, the authors describe some observations of cases of suspected poisoning with atropine, and their experiments with animals and solutions of atropine, from which they draw the following conclusions:—(1.) Vitali's reaction for atropine is only slightly less sensitive than the mydriatic action, 0·0000002 gram being the smallest amount that can be distinctly detected by the former method; rabbits dosed with slightly less than this amount should be kept under observation for at least half an hour. (2.) The changes which an aqueous solution of atropine undergoes (Flückiger, *Pharm. Chem.*, 1888, 542) are accelerated by exposure to light, and probably by dilution and a moderately high temperature; free atropine is more readily altered than its salts, and the product in any case does not respond to either the chromatic or the physiological test. (3.) In the extracts from two human bodies, obtained by the Stas-Otto method, Vitali's reaction was obtained in the absence of atropine; some ptomaïne capable of giving this reaction must therefore exist in putrefied animal remains. (4.) It appears that purification of the extracts, whilst removing a considerable portion of the atropine when present, only partially removes this ptomaïne.

The authors hold that in medico-legal investigations evidence of the presence of a poison cannot be considered conclusive unless its characteristic chemical reactions, together with its physiological effects, are severally and satisfactorily exhibited.

S. B. A. A.

General and Physical Chemistry.

Relations between the Lines of Various Spectra. By W. N. Hartley (*Phil. Mag.* [5], **31**, 359—363).—A reply to some criticisms on the author's work by J. S. Ames (this vol., p. 2). J. W.

Absorption Spectrum and Colour of Liquid Oxygen. By K. Olszewski (*Ann. Phys. Chem.* [2], **42**, 663—665).—In his former examination of the absorption spectrum of liquid oxygen (Abstr., 1887, 625), the author found bands corresponding with the wave lengths 628, 577, 535, and 480. Liveing and Dewar (Abstr., 1891, 1), on examining the absorption spectrum of gaseous oxygen under high pressure, found the same four absorption bands in the visible part of the spectrum, and also two bands in the extreme red corresponding with the Fraunhofer lines A and B.

The author has lately had occasion to prepare liquid oxygen in some quantity and has repeated his examination of the absorption spectrum, more particularly in the extreme red. The column of liquid oxygen obtained had a thickness of 30 mm., and was 50 mm. in height. It was contained in a thin glass vessel surrounded by three glass beakers, in order to protect it, as far as possible, from outside heat. In this condition it was found possible to keep a sufficient quantity for the purpose in view, under atmospheric pressure and at its boiling point −181·4°, for over half an hour. The observations gave the four absorption bands before obtained, and also a fifth corresponding with the Fraunhofer line A. This band is of less intensity than those of wave-lengths 628, 577, and 480, but stronger than the band 535. An absorption band corresponding with the Fraunhofer line B was not observed.

Liquid oxygen, as first obtained in small quantity in 1883, was described as being colourless. Since then the author has repeatedly had under examination liquid oxygen in larger quantities, and he has invariably noticed that a layer of greater thickness than 15 mm. has a distinctly blue colour by transmitted light. In the above experiments, in which liquid oxygen was employed in larger quantity than had hitherto been the case, the pale-blue colour of the liquid was particularly noticeable. As special precautions were taken in purifying the gas, and the absence of ozone was ascertained by special tests, there seems no reason to doubt that the colour observed is characteristic of oxygen in the liquid state. In the author's opinion, the blue colour of the sky is therefore probably due to the oxygen in the atmosphere, since this element, at any rate in the liquid condition, is blue in colour. H. C.

New Method of Investigating Faint Bands in Spectra; Spectra of Hydrocarbons. By H. Deslandres (*Compt. rend.*, **112**, 661—663).—The bands λ 438·19, λ 437·13, and λ 436·5 observed, together with the ordinary bands of hydrocarbons and of cyanogen, in the electric arc and in the combustion of cyanogen, have been variously attributed to cyanogen and to hydrocarbons. The application of the method of calculation previously described (Abstr., 1888, 637), shows that from the known 16 bands of hydrocarbons the positions of the three bands in question can be accurately calculated, and hence the author concludes that they really belong to the hydrocarbons. Calculation indicates the presence of bands at λ 408·35 and λ 408·17, but they will be very feeble, and will be more or less hidden by the intense bands of cyanogen. C. H. B.

Refraction and Dispersion of Fluorobenzene and Allied Compounds. By J. H. Gladstone and G. Gladstone (*Phil. Mag.* [5], **31**, 1—9).—The following table contains the index of refraction of fluorobenzene, as determined by the authors, for the principal lines of the solar spectrum, together with the customary optico-chemical values deducible from these numbers. The temperature of observation was 22·8° :—

	A.	C.	D.	F.	G.	H.
Refractive index, μ	1·4563	1·4606	1·4646	1·4751	1·4849	1·4933
Molecular refraction, $\frac{\mu - 1}{d}$ M......	42·92	43·33	43·70	44·68	45·61	46·40
Atomic refraction of fluorine	0·63	0·63	0·53	0·48	0·44	0·35

It thus appears that the atomic refraction of fluorine in organic compounds is very small compared with that of chlorine, bromine, and iodine, the values for which are 10·00, 15·23, and 25·20 respectively for the line A. The atomic dispersion of fluorine, too, is anomalous, the refraction being less at the blue end of the spectrum than at the red. A consideration of various inorganic fluorides served to confirm the above results with regard to the optical properties of fluorine. J. W.

Dispersion of Carbon Compounds: Ethereal Salts. By P. Barbier and L. Roux (*Compt. rend.*, **112**, 582—584; compare Abstr., 1890, 1353).—In the ethyl salts of acids of the acetic series, and in the acetates of the radicles of the methyl series, allyl, and benzyl, the specific dispersion increases with the molecular condensation. The mean difference between the molecular dispersive powers of two consecutive homologues is practically constant, and is equal to 7·5. The molecular dispersive power of the alkyl salts is equal to the algebraic sum of the molecular dispersive powers of its components. Isomerides, such as ethyl formate and methyl acetate, have very different dispersive powers. C. H. B.

Relations between Dispersion and Chemical Constitution. By J. W. Brühl (*Zeit. physikal. Chem.*, **7**, 140—193).—After giving a short historical survey of the work already done on the optical dispersion of organic substances, the author proceeds to discuss the merits of the various dispersion constants which may be adopted. He rejects the expression for the specific dispersive power used by Barbier and Roux, namely, $\frac{B}{d}$, where B is the second member of Cauchy's dispersion formula, and d the density (Abstr., 1890, 673), on the ground that it is theoretically without foundation and inexact in practice; and prefers to follow the example of Gladstone, who simply subtracts the specific refractive powers for two different wavelengths in order to obtain the specific dispersive power. Instead however, of employing the empirical refraction constant, $\frac{n-1}{d}$, used by Gladstone, he takes the "theoretical" constant $\frac{n^2-1}{(n^2+2)d}$, so that his expression for the molecular dispersive power becomes

$$\left(\frac{n_\gamma^2-1}{n_\gamma^2+2}-\frac{n_\alpha^2-1}{n_\alpha^2+2}\right)\frac{M}{d};$$

the light used being H_α and H_γ (Fraunhofer, C and f). This formula is practically independent of the temperature, and varies only very slightly even when the substance passes from the liquid into the gaseous state, which gives it the preference over Gladstone's formula.

From the data available for isomeric substances of the fatty series with similar distribution of valencies, it follows that the position of the atoms in the molecule has little, if any, influence on the dispersive power: on the other hand, if the distribution of the valencies is different in two isomeric substances (for example, allyl alcohol and propaldehyde) then the specific and molecular dispersive powers are also different.

The following homologous series of C_nH_{2n+2} or paraffinoïd derivatives were investigated:—alcohols, ethers, bromides and iodides, aldehydes, ketones, acids, ethereal salts, and acid chlorides. It was found that in all these series there is a constant difference in molecular dispersive power for a difference in composition of CH_2: the value ranges from 0·104 (aldehydes) to 0·119 (iodides), and is in the mean 0·110.

In the case of the olefines and benzene derivatives, the difference is not constant, but as the data here are limited no safe conclusion can be drawn.

The author, from the material he has collected, revises the values for the atomic refractive powers to be attributed to the elements, and also gives numbers for the atomic dispersion. He distinguishes between oxygen united to 2 atoms of carbon (ether oxygen) and oxygen united to 1 atom of carbon and 1 of hydrogen. The following table contains his results (p. 776).

It is thus apparent that the dispersive power is essentially additive in character, but profoundly modified by structural influences. A glance at the table further shows that there is no simple relation between the refractive and the dispersive power of substances.

	Atomic refraction.		Atomic dispersion.
	Old values.	Revised values.	
Singly bound carbon	2·48	2·365	0·039
Hydrogen	1·04	1·103	0·036
Hydroxylic oxygen	1·58	1·506	0·019
Ether oxygen		1·655	0·012
Carbonylic oxygen	2·34	2·328	0·086
Nitrogen (singly bound to carbon only)	3·02	2·76	0·19
Chlorine	6·02	6·014	0·176
Bromine	8·95	8·863	0·348
Iodine	13·99	13·808	0·774
Ethylene linking	1·78	1·836	0·23
Acetylene linking	1·97	2·22	0·19

The data for the olefines and the derivatives of benzene throw no light on the distribution of the bonds in the latter: one can only say that the nucleus is certainly not held together by nine ordinary fatty bonds. A few cinnamyl compounds were investigated. These substances have an abnormally high dispersive power, and this the author is inclined to attribute, with Gladstone, to the presence in them of an unsaturated carbon atom directly bound to the benzene nucleus. When a carbonyl group is linked to an unsaturated carbon atom, as in acraldehyde, the dispersive power is here also unusually great. J. W.

Optical Properties of α-Bromonaphthalene. By B. Walter (*Ann. Phys. Chem.* [2], **42**, 511—512).—α-Bromonaphthalene, in addition to having a strong dispersive power, is very transparent to ultra-violet rays. This combination of optical properties makes the substance an important one in researches on fluorescence, phosphorescence, &c. The coefficient of refraction alters comparatively little with the temperature. J. W.

Phosphorescence of Minerals under the Influence of Light and Heat. By H. Becquerel (*Compt. rend.*, **112**, 557—563).—Various forms of fluorspar from various sources were excited by light, heat, and the electric spark, and the spectrum of the phosphorescence was examined. Measurements of the wave-lengths of the bands are given. In the phosphoroscope, the bands that are visible or have the highest intensity vary with the speed of rotation of the disc, a result due, according to the author, to differences in the persistence of the phosphorescence of the various substances that are present in the fluorspar and give rise to the different spectra. The electric spark excites phosphorescence in the same way as sunlight, and the spectra are the same; the effect is more intense with the spark than with sunlight, probably because of the high proportion of rays of high refrangibility in the former. When the fluorspar is heated, a limited quantity of energy is set free in the form of luminous vibrations, but if the heating is continued, the phosphorescence ceases. It can, however, be restored by exposing the substance to light or the electric spark. The bands in the spectrum when the substance is heated, have the same positions as in the phosphoroscope, but they have different relative intensities. The relative intensities also vary with the temperature. Phosphorescence under the influence of heat belongs in fact to the same class of phenomena as phosphorescence excited by light. C. H. B.

Experiments with Selenium Cells. By S. BIDWELL (*Phil. Mag.* [5], **31**, 250—256).—Selenium cells made in the manner suggested by the author (*Nature*, **23**, 58) gradually lose their great resistance and also their sensibility to light. Only one cell out of 13 retained its original sensitiveness over a space of 10 years. A current from a 26-volt battery, passed through a selenium cell with copper electrodes for two days, deposited amorphous selenium and an oxide of selenium at the anode. The resistance of the cell was then different, according as the current passed from anode to cathode or from cathode to anode. When a piece of magnesium ribbon was burnt near this cell, a current from anode to cathode was indicated by the galvanometer, which ceased when the light was extinguished. The current was proved not to be due to thermoelectric action.

J. W.

Chemistry of Secondary Batteries. By J. H. GLADSTONE and W. HIBBERT (*Phil. Mag.* [5], **31**, 42—44).—Frankland (Abstr., 1890, 842) has contended that the lead compounds which play the chief part in the chemical reactions taking place on the charging and discharging of secondary cells are subsulphates. The authors have already shown that one of these is not a definite compound (this vol., p. 3), and now prove that the second substance, $Pb_3S_2O_{10}$, derived from sulphuric acid and red lead, may be decomposed by a solution of ammonium acetate, which dissolves out lead sulphate and leaves behind lead peroxide.

An analysis of the residue left by the action of pure dilute sulphuric acid on spongy lead during a period of five months, gave the composition 82 per cent. lead sulphate, and 18 per cent. metallic lead. Only 11 per cent. of metallic lead remained when the acid in a similar experiment was mixed with sodium sulphate. J. W.

Electrical Phenomena Developed in the Formation of Solid Carbonic Oxide. By G. HAUSSKNECHT (*Ber.*, **24**, 1031—1032).—Solid carbonic oxide is easily obtained by allowing the liquid compound contained in an iron cylinder to evaporate rapidly into a bag of sail cloth. When a bag of 1—2 litres capacity is employed, and the experiment conducted in the dark, a pale, greenish-violet light is observed in the bag, and electric sparks of 10—20 cm. in length shoot out through the pores of the bag. If the hand is brought in contact with these sparks, the same pricking sensation is felt as is produced by an electrical machine. The cause of these electrical phenomena is probably the same as in Armstrong's gas electric machine. The carbonic oxide as it rushes out from the cylinder is pressed rapidly through the fine openings in the sides of the bag, and thus is strongly rubbed, and also causes small quantities of the liquid and solid to rub together. An essential condition for success is the absence of air in the carbonic oxide employed. The phenomenon of light is first developed when a crust of solid carbonic oxide of 0·5—1 cm. has formed in the bag. The author is engaged in investigating the nature of the phenomena and determining the quantity of electricity developed. E. C. R.

Specific Inductive Capacity of Electrolytes. By E. B. Rosa (*Phil. Mag.* [5], **31**, 188—207).—The author studied the specific inductive capacity of water and alcohol by measuring the force exerted between a fixed and a movable electrode in an electrolytic cell. The following is a summary of his results :—

(1.) The expression for the force between two electrodes having a homogeneous medium between them is of the form $F = AKV^2$, where F is the force, A a constant, K specific inductive capacity of the medium, and V potential. For a given liquid and given electrodes at a constant distance, F is proportional to V^2. This holds for electrolytes as well as dielectrics through a range of potential from 1 to 60 volts.

(2.) When the potentials and medium are constant, and the distance between the electrodes is varied, F is independent of the nature of the medium, depending only on the capacity of the condenser.

(3.) When the rate of alternation of the current changes, the force is but slightly altered, unless the electrolyte is a fairly good conductor. In the latter case, the force is diminished if the speed is reduced, owing to polarisation.

(4.) When the conductivity of distilled water is increased by the addition of tap water, or of minute quantities of acid or of copper sulphate, the force is not greatly altered, although the current increases many times. The slight decrease observed is probably due entirely to polarisation.

(5.) With rise of temperature, the conductivity increases while the force diminishes, the rate being practically constant within the range of experiment. This diminution is not due to polarisation, for the increase of conductivity is comparatively small, and a slight fall of temperature conditions an immediate and full restoration of the force.

The electrolytes considered behave therefore very much as dielectrics. The following values of K were obtained at 25° C :—For water, $K = 75·7$; for alcohol, $K = 25·7$. These determinations agree with the work of Cohn and Arons and others. J. W.

Electrolysis. By F. Braun (*Ann. Phys. Chem.* [2], **42**, 450—464).—Grotthus (*Gilbert's Annalen*, **61**, 65) passed an electric current through two solutions of silver nitrate, communicating with each other only by means of a crack in the glass tube containing one of them. The positive pole was immersed in the external vessel. He observed that silver was deposited on the outside of the crack, whilst oxygen was given off on the inside. The author has now made a series of experiments which confirm this observation. He finds that the silver is only deposited when the intensity of the current has attained a certain minimum value which depends on the strength of the solution.

The corresponding phenomenon was not observed with manganese and nickel salts, but salts of lead, gold, palladium, cobalt, and iron showed it distinctly. Formation of a peroxide which might conduct as a metal seems to be without influence in producing the electrolysis.

As the current passes, bubbles of gas may be seen in process of formation in the crack, which pulsates as the bubbles increase in size and are liberated on reaching the surface. This may be also noticed with acids and alkaline salts. In the dark, sparks may be observed within the crack. The breadth of the crack need not be very small, as the phenomena of electrolysis were observed at a slit of 0·06 mm. breadth cut in a mica plate.

The author considers the sparks to be due to the recombination of the oxygen and hydrogen liberated on the passage of the current. Further experiments on the subject are promised. J. W.

Influence of Temperature and the State of Aggregation on the Behaviour of Bismuth in the Magnetic Field. By P. Drude and W. Nernst (*Ann. Phys. Chem.* [2], **42**, 568—580).—The Hall phenomenon of the rotation of the equipotential lines by a galvanic current, in the case of bismuth is found to be less marked at a temperature just below the melting point than at the ordinary temperature. Above the melting point the effect is so slight as to have become scarcely measurable. On allowing the bismuth to solidify and cool down again, it did not return exactly to its initial condition as measured by the Hall effect. The increase in the resistance of bismuth in the magnetic field also becomes smaller with rising temperature. The increase in this case already becomes very slight at a temperature much below that at which bismuth melts. The bismuth does not return to its initial resistance on cooling.

Antimony was also examined with somewhat similar results, the effect of change of temperature being, however, far less marked than in the case of bismuth. In the case of mercury, the Hall effect could not be measured, and although a distinct increase of resistance was noticed, the influence of temperature was not ascertained.

Bismuth, as far as could be ascertained, undergoes no change in optical properties in the magnetic field. H. C.

Determination of Critical Temperatures and Pressures, especially that of Water. By L. Cailletet and H. Colardeau (*Compt. rend.*, **112**, 563—565).—In order to eliminate the action of water or other liquids on glass, and to avoid the necessity for observing the meniscus, the liquid is placed in a metal tube connected with a manometer. Varying quantities of the liquid are used, and the apparatus is heated to definite temperatures and the pressure observed. If the quantity of liquid is insufficient to fill the apparatus even when it has expanded, but is sufficient to furnish a saturated vapour, the pressure of the saturated vapour is the same at any given temperature below the critical point, whatever may be the weight of the liquid in the apparatus. Beyond the critical point, however, the pressures are different for each particular weight of liquid in the apparatus. The determination of the critical point, therefore, resolves itself into a determination of the temperature at which the curve of pressure with different quantities of liquid in the apparatus ceases to be independent of this quantity. Details of the measurements in the case of water will be published after the manometer has been verified by means of a special manometer at the Eiffel tower.

C. H. B.

Specific Gravity of a Liquid a Function of its Boiling Point and Molecular Weight. By A. E. Richardson (*Chem. News*, **63**, 58—60).—The boiling point of a liquid has been shown to be to some extent dependent on its molecular weight, but hitherto between specific gravity and the temperature of ebullition no definite relations seem to have been observed. In this paper, the author endeavours to show the existence of such relations, considering only those liquids which have a specific gravity greater than unity.

Imagine the case of a liquid heated to temperatures far above its boiling point. Also conceive that ebullition has by some means been prevented. Under such circumstances it is palpable that the specific gravity of the liquid will have much decreased, taking it for granted that the liquid would continue expanding. At some temperature, constant for each liquid, the specific gravity would at last assume unit value. Here, then, is a new condition of liquid matter, namely, the temperature at which each given liquid attains unit specific gravity. To arrive at these temperatures, two measurements are required for every liquid. We must know the specific gravity at some given temperature, and the rate of expansion between 0° and the boiling point.

From existing data, the values of T, the unit specific gravity temperature, and of $T\alpha$, the absolute temperature of unit specific gravity, are calculated for a number of liquids. Plotting these values as ordinates against the specific gravities as abscissæ, regular curves are obtained, showing that specific gravity is a function of the temperature of unit specific gravity. The values of T/m, where m is the molecular weight, are very uniform, and many of them closely approximate to the number 2. Hence, since T/m approaches constant value, the temperature of unit specific gravity varies as the molecular weight, and the specific gravity is therefore a function of the molecular weight. Lastly, there is a greater uniformity between the values of $T\alpha/t\alpha$, where $t\alpha$ is the absolute temperature of boiling, than between those of T/m, and consequently all that has been said with regard to the values of the latter applies with even greater force to values of $T\alpha/t\alpha$.

H. C.

Laws of Dissociating Gases. By A. J. Swart (*Zeit. physikal. Chem.*, **7**, 120—139).—The fundamental equations for ideal gases are put into the following form, in order to take into account the volume of the molecules and their attraction for each other :—

I. Physical equation.... $\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{T}\Sigma\mathrm{R}.$

II. Chemical ,, ... $\mathrm{K} - \frac{q}{\mathrm{T}} = \Sigma n \log_e \mathrm{C}.$

R is the gas-constant for each constituent of the dissociating mixture, n the number of molecules of each constituent that participate in the reaction producing equilibrium, C the corresponding concentration, q the internal heat transformation per half kilogram molecule, and K a constant of integration.

The case of nitrogen peroxide is first studied, the proper values being inserted in the above equations, and the law for the dissociation deduced from them. Natanson's experimental results compared with the calculated values show a fair agreement.

The equation obtained is then applied to the investigation of the coefficient of tension, the coefficient of expansion, the critical temperature, the specific heat, and the velocity of sound in dissociating nitrogen peroxide. In these cases also the accordance of theory with experimental results is satisfactory. Applications to other dissociating gases are also made. J. W.

Constant Vapour Pressure. By J. L. ANDREAE (*Zeit. physikal. Chem.*, **7**, 241—273).—It is a well-known fact that the vapour pressure of any hydrated crystalline salt alters with the amount of water the salt contains, that of $CuSO_4,3—5H_2O$ being greater than that of $CuSO_4,1—3H_2O$, and that of the latter in its turn greater than $CuSO_4$ with less than 1 mol. of water. Whether the alteration is more or less gradual, or whether it takes place in an abrupt manner as the proportion of the water to that of the salt is increased, has not yet been ascertained, and the object of the present paper was to obtain an answer to this question.

Two methods of observation were employed, the one statical, and the other dynamical. In the statical method, two samples of the same salt in different degrees of hydration were enclosed in vacuous bulbs connected by means of a U-tube filled with oil, which served as a manometer for indicating and measuring an excess of pressure in either bulb. By means of this apparatus, experiments could be conducted at various temperatures. In the dynamical method, two bulbs were taken, and, as before, filled with different samples of the hydrated salt. Each was weighed separately, and the two then so connected as to allow a free passage of water vapour from the one bulb to the other, both being perfectly shut off from the outside air. Under these circumstances, water passes from the salt of higher to that of lower tension, this continuing until equilibrium is established, a change which is readily ascertained by disconnecting and weighing the bulbs from time to time. When the weights become constant, the salts in each bulb are analysed, and the change which has taken place determined quantitatively.

Three salts were examined, strontium chloride, copper sulphate, and sodium carbonate. With the first of these salts, three experiments were first of all conducted by the dynamical method. The two bulbs contained in the three cases $SrCl_2,5\cdot8H_2O$ and $5\cdot0H_2O$, $SrCl_2,5\cdot8H_2O$ and $3\cdot4H_2O$, $SrCl_2,5\cdot8H_2O$ and $2\cdot6H_2O$. They were left connected with one another for 66 days, and weighed from time to time. No change of weight in any of the bulbs was noticed during or at the end of this time. The conclusion is that no unequal exchange of water had taken place between the above salts, and that their vapour pressures are therefore the same. Two experiments were now conducted in which the bulbs contained $SrCl_2,5\cdot8H_2O$ and $1\cdot65H_2O$, and $SrCl_2,5\cdot8H_2O$ and $0\cdot6H_2O$. These bulbs were left connected in all for 200 days. In the first pair, a passage of water from the salt of higher to that of lower hydration took place during the first 19 days, and after this no further change occurred. In the second pair, a similar change took place, and was completed in about 50 days. On analysing the salts at the end of the experiments, they were found to have the composition $SrCl_2,5\cdot42H_2O$ and $2\cdot01H_2O$, and $SrCl_2,4\cdot01H_2O$ and $2\cdot01H_2O$. From this it appears that $SrCl_2,5\cdot8H_2O$ has a greater tension than a salt containing less than $2H_2O$; but from what has gone before it appears that its tension is not greater than that of any salt containing more than $2H_2O$. Between $SrCl_2,2H_2O$ and $SrCl_2,6H_2O$ no increase, therefore, in the vapour pressure of the hydrated salt takes place, but salts of all intermediate compositions have the same vapour pressures. This result was confirmed by the statical method, in which case salts of composition between those above quoted were enclosed in the two bulbs of the apparatus, and the pressure in the two was found to remain equal. Variation in temperature made no difference in the result as long as the heating of both bulbs was the same. On the other hand, when a salt containing more than $2H_2O$ was enclosed in one bulb, and a salt containing less than $2H_2O$ in the other, a very distinct excess of pressure was noticed in the former bulb, the difference becoming more pronounced as the temperature was raised. Experiments were also made to ascertain whether $SrCl_2,2H_2O$ has a greater tension than $SrCl_2,H_2O$, but with negative result.

The investigation of the behaviour of the other two salts was carried out in a perfectly similar manner. It was found that the tension of $CuSO_4,3—5H_2O$ was greater than that of $CuSO_4,1—3H_2O$, and that the latter is greater than that of $CuSO_4$ with less than 1 mol. of water. Between the limits given here, however, the vapour pressures remain constant, so that the pressure does not change gradually, but undergoes an abrupt alteration at $CuSO_4,H_2O$ and $CuSO_4,3H_2O$. In the case of sodium carbonate, there is no change in the vapour pressure between Na_2CO_3,H_2O and $Na_2CO_3,4\cdot5H_2O$, as also between $Na_2CO_3,6\cdot95H_2O$ and $Na_2CO_3,10H_2O$. The experiments do not serve, however, to determine the exact composition of the intermediate hydrate.

From the above it is evident that the vapour pressures of salts of different hydration are equal when the salts contain an amount of water which is either above or below a certain limit. In the cases considered the limits are $SrCl_2,2H_2O$, $CuSO_4,H_2O$, and $CuSO_4,3H_2O$, Na_2CO_3,H_2O, and probably $Na_2CO_3,6\cdot7H_2O$. On the other hand, the vapour pressures of salts of different hydration are unequal when one salt contains an amount of water which is greater, and another salt an amount of water which is less, than a certain limit. It is, therefore, obvious that the vapour pressure of any hydrated salt will not change regularly with the degree of hydration, but that the change will be abrupt and occur at certain intervals. H. C.

Vapour Pressure of Copper Potassium Chloride and its Solutions. By J. G. C. VRIENS (*Zeit. physikal. Chem.*, **7**, 194—220).—This research is supplementary to those of Meyerhoffer (Abstr., 1889, 819, and 1890, 564), who investigated the reciprocal transformations of the various compounds of cupric chloride with potassium chloride, and the solubility of the systems composed of these substances. The author has now made a complete set of corresponding determinations of the vapour pressures of the solid compounds and of their saturated solutions. He finds, in confirmation of Meyerhoffer's work, that the vapour pressure at the temperatures of transformation of one system into another is always the same, irrespective of the composition of the mixture; and has succeeded in many cases in pursuing the curves of vapour pressure into the unstable region beyond the point of transformation.

In order to compare his results with the deductions from thermodynamical theory, he determined the heat of combination of the water of crystallisation in the compounds, and calculated the vapour tensions by means of the formula $\frac{d \log_e F}{dT} = \frac{Q}{2T^2}$, where F is the ratio of the maximum pressure of the vapour from the water of crystallisation to that of pure water; T the absolute temperature, and Q the heat developed by the combination of 18 kilos. of water. The theoretical and experimental numbers are in satisfactory agreement. J. W.

Vapour Pressures of some Aqueous Salt Solutions at 0°. By C. DIETERICI (*Ann. Phys. Chem.* [2], **42**, 513—536).—In a former paper (Abstr., 1890, 207), it has been shown that saturated water vapour at 0° obeys the ordinary gaseous laws and the pressure which it exercises was calculated from measurements of the density. The vapour pressures of some salt solutions have now been determined in like manner, and the reduction of the vapour pressure of the water by the addition of the salt thus ascertained. The method used was, as before, calorimetrical, the weight of water converted into vapour and occupying a certain known volume being determined by measuring the heat of vaporisation.

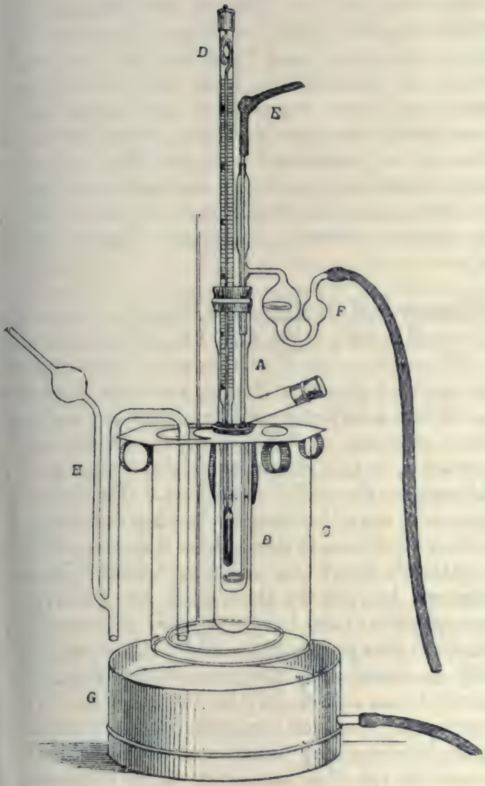
The salts examined were sodium chloride and nitrate, potassium chloride, bromide, and iodide, and lithium chloride. In the case of the potassium salts, the reduction in the vapour pressure of the water was found to be very nearly proportional to the amount of salt present. With sodium nitrate, the vapour-pressure reduction decreases; with sodium chloride, and still more with lithium chloride, it increases more rapidly than the amount of salt. It is, therefore, evident that the alteration of vapour pressure with the amount of dissolved salt is different for different salts at 0°, as has already been shown to be the case for other temperatures by Tamman and Emden (Abstr., 1887, 764). Since the ratio of a vapour pressure of the solution to that of pure water should, according to Babo's law, remain unchanged by temperature, a comparison of the author's results for 0° with those of Tamman for 100° is made, and the above law is found to hold good with remarkable accuracy.

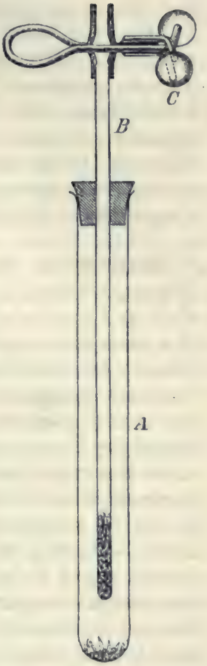
According to the Van't Hoff theory, the vapour-pressure reduction should be proportional to the amount of salt present, or accepting the dissociation hypothesis of Arrhenius, should decrease with increasing concentration. The results with sodium and lithium chlorides are, however, in direct opposition to the latter view, which only those obtained with sodium nitrate support. The author calculates the values of Van't Hoff's coefficient i from his results, and compares them with those obtained by Arrhenius from the electrical conductivities and the reduction of the freezing point. The agreement is far from satisfactory. Two non-electrolytes, cane-sugar and urea, were also examined, and for these values for i of 1·08 and 0·84 were obtained.

H. C.

Apparatus for Freezing Point Determinations. By E. BECKMANN (*Zeit. physikal. Chem.*, **7**, 323—330).—The apparatus, of which a sketch is here given, is a slightly modified form of that described by the author in a former paper (Abstr., 1889, 11). It consists of the inner vessel A, surrounded by the air-jacket B, and placed in a cooling solution or mixture in the outer vessel C. Into A a weighed quantity of the solvent is introduced. This is done by weighing the liquid in a Sprengel U-tube, transferring it to A through the side tube on the right, and then weighing the empty Sprengel tube. After the freezing point of the solvent has been ascertained in the usual manner, a weighed quantity of the substance which is being experimented with is introduced through the side tube into A, and after it has all been dissolved by the solvent, the freezing point of the solution is ascertained. The difference between this and the former determination gives the freezing point reduction.

The thermometer D registers only in all about 6° and is graduated to $\frac{1}{100}^{\circ}$. As absolute measurements are not required, it can be adjusted for use with any solvent by means of a small reservoir at the top, to or from which some of the mercury can be removed at will, so that the readings shall fall on suitable portions of the scale. A stout piece of platinum wire, introduced through a glass tube in the cork carrying the thermometer, serves as a stirrer. When a very hygroscopic substance is used as the solvent, it is advisable to pass a stream of air, dried by being passed through sulphuric acid in the bulbs F, through the space between the stirrer and the glass tube. The india-rubber tube E, fastened to the upper portion of the stirrer, enables the operator to secure a firm grasp of the latter. When dealing with hygroscopic substances, the apparatus should be closed with tightly-fitting india-rubber stoppers. On introducing the material experimented with into the apparatus, it sometimes happens that a portion remains adhering to the side tube, the thermometer, or the stirrer. The inner tube should then be removed from the vessel B, and inclined, so that the solvent enters the side tube, and, after dissolving the substance remaining in this, is made to wash the stirrer and thermometer when the tube is returned to its original position.





In liquids which do not readily crystallise, crystallisation may be induced by introducing a small quantity of the previously crystallised solvent. In the tube A of the sketch, a small quantity of the solvent is placed, and after being drawn into the tube B, closed at the top by means of the pinch-cock C, it is submitted to a temperature sufficiently low to cause crystallisation. On withdrawing B from A, and warming slightly, the solid becomes sufficiently detached to allow a small portion to fall from the tube on opening the pinch-cock. B is then replaced in A, and left in the freezing mixture until again required.

The above apparatus may be employed not only with substances solidifying at low temperatures, but also with solvents which are themselves solid at ordinary temperatures. The author quotes experiments with phenol and with naphthalene as solvents in illustration of this, in which cases the outer vessel C was replaced by a beaker filled with water and by means of a thermostat kept constantly at a temperature a little below that at which the solvent melts.

H. C

Thermal Potential for Dilute Solutions. By E. RIECKE (*Ann. Phys. Chem.* [2], **42**, 483—501).—The author, taking the fundamental equation of Gibbs as his basis, calculates the potential for the components of a dilute solution; and then applies his results to the consideration of various phenomena that such a solution exhibits. He thus deduces the laws regulating the lowering of vapour pressure, the depression of the freezing point, dissociation of electrolytes, the distribution of a substance between two solvents, osmotic pressure, diminution of solubility, and the absorption of gases. The results he obtained are identical with those got experimentally, or derived theoretically by other methods (compare Planck, *Ann. Phys. Chem.* [2], **32**, 485). J. W.

Discussion on the Theory of Solution (*British Association Report*, 1890, 311; *Chem. News*, **62**, 185, 194; **63**, 147, 157, 169; and *Zeit. f. Physikal. Chem.*, **7**, 378—426).—S. U. PICKERING (who opened the discussion with a paper on the "Present Position of the Hydrate Theory of Solution") said: When a definite solid hydrate crystallises from a solution, the existence of some molecules of this hydrate in the liquid can scarcely be denied, but it does not follow that every liquid hydrate can be obtained in the solid condition. Evidence of such uncrystallisable compounds must be sought in the existence of irregularities in the properties of the solution when its composition is varied regularly. The author's work on sulphuric acid (Trans., 1890, 338) and other substances, has shown that such irregularities, consisting of definite changes of curvature in the figures representing the various properties, exist, that the position at which they occur is the same whatever property is examined, and, moreover, that this position corresponds wherever it can reasonably be expected to do so, with simple molecular proportions. Similar irregularities are noticed with very weak solutions, indicating the existence of hydrates of great complexity. The lowering of the freezing point of several solvents must, even on the physical theories, lead to the conclusion that liquid molecules are often very complex. A careful examination of the freezing points shows that the molecular depression (that produced by one molecule dissolved in 100 molecules of solvent) is by no means a constant, but varies with the nature of the solvent and of the dissolved substance, and also varies irregularly with the strength of the solution, even when this is very small, and when the dissolved substance is not an electrolyte. Such variations and irregularities can only be attributed to the existence of disturbing causes (such as hydrates), and they are inconsistent with any purely physical theory of solution. The depression with very strong solutions is generally abnormally large, whereas according to the physical theory the reverse should be the case. With every solvent there are instances of substances which on dissolution produce only half the normal depression of the freezing point, this abnormal action being attributed to the acting molecule consisting of two fundamental molecules; in the case of water the smaller values are regarded as normal, and the larger as abnormal, their abnormality being due to the dissociation of the molecule into two or more ions. This view is irreconcilable with Raoult's constant of 0·63° for the molecular depression, for the smaller value in the case of water is 1°·03, and this would necessitate the acting molecule of water being $\frac{1·03}{0·63}$, or $1\frac{1}{2}H_2O$. Other objections are raised against the dissociation theory; thus, the stability as evinced by the heat of formation as well as by the chemical properties of many of the substances said to be dissociated, is contrasted with the instability of many of those which are represented as remaining intact: again, the heat evolved in the dissolution of hydrochloric acid cannot be attributed to dissociation into ordinary atoms (for such a dissociation must absorb heat), and it has, therefore, to be attributed to the combination of electric charges with the atoms, a view which endows an electric charge with an attribute possessed, as far as we know, by matter only. Ostwald's experiment of producing electrolysis by a current of electrostatic origin cannot prove the pre-existence of free ions in solution, for, if the conservation of energy is to hold, energy in some form must have been expended on the solution, and there is nothing to show that it has not been utilised in bringing about the decomposition of the molecules. An outline is then given of the views which the author has propounded as to the freezing points of solutions, according to which, by taking into account the existence of hydrates as well as the mechanical effect produced by introducing foreign molecules into a solvent, the depression of the freezing point of water by sulphuric acid may be calculated as far as −34°, or 30 per cent. (Proc., 1889, 149); the concordance is so good that the composition of the hydrates may be calculated from the observed freezing points, and these hydrates are found to agree with those indicated by the study of the curves representing the various properties of the solutions. In the case of weak solutions, the lowering which can be attributed to chemical causes alone is but a small portion of the total lowering, and this accounts for the approximate regularity and constancy observed with such solutions, and the approximate validity of calculations based on purely physical views, even though solutions may be truly chemical in their origin and nature.

J. H. GLADSTONE said that substances generally have the same molecular refraction in whatever solvent they are dissolved, and a solution has the same specific refractive energy as the mean of those of the solvent and the dissolved substance: ammonia dissolved in alcohol has, moreover, the same value as gaseous ammonia. Water as a solvent behaves anomalously; the haloïd salts exhibit a higher refraction and dispersion in water than that given by calculation; in water, also, the refraction increases with dilution up to a certain extent and then becomes constant, whilst in other solvents dilution has no effect; this difference the speaker considered was evidently not dependent on the dissolved substance being an electrolyte or not. With hydrochloric acid, he had obtained results analogous to W. H. Perkin's magnetic rotation results; in isoamyl oxide, the acid gives the theoretical value (11·25); in water, it gives a value 3·15 higher; as free chlorine and hydrogen would give a smaller value than the compound, and as the addition of water of hydration would probably not affect the value at all, no conclusions in favour of either the dissociation or the hydration theory can be drawn from these results, and the speaker could only infer that some profound and at present unknown change is effected on the constitution of many substances by dissolving them in water.

S. Arrhenius communicated a statement to the effect that a decrease in the molecular depression of the freezing point with an increase of concentration was not a consequence of the law of osmotic pressure. Yet Beckmann's and Eykman's determinations show that such a decrease occurs in the majority of cases. Owing to electrolytic dissociation, the molecular depression should not be a constant independent of concentration in the case of weak solutions of electrolytes. Taking a certain value for the conductivity of an infinitely dilute solution of sulphuric acid, he showed that the calculated depression agrees with Pickering's observed values within experimental error as far as a strength of 1 per cent., or a depression of 0·4°, and fairly well as far as 4 per cent., or 1·6°.

J. Walker said that Arrhenius' objection, that electrolytic dissociation had not been taken into consideration, applied to almost all of the instances tabulated by Pickering.

W. Ramsay suggested that it was not inconceivable that complexes of the dissolved substance, compounds of the latter with the solvent, and also the ions resulting from its dissociation, might all coexist in solution.

H. E. Armstrong said that the dissociationists regarded the neutralisation of an acid by an alkali as consisting solely of the formation of water from some of the ions constituting the reagents. Water and hydrochloric acid are thus regarded as being compounds of a totally different order, the former undissociated, the latter nearly entirely dissociated, a proposition opposed to known facts of chemistry, and also to the behaviour of these substances at high temperatures. He considered that the numerical agreements between theory and practice did not prove the correctness of the dissociation theory; electrical resistance was, no doubt, a measure of the activity of a substance, and it could, therefore, be successfully used in applying a correction for the superior activity of compounds in various cases, but this superior activity might be either chemical or physical in its nature.

G. Fitzgerald said that there must necessarily be a connection between many physical properties. The connection between electric conductivity and osmotic pressure was a very important one, and he proposed that the quality measured by the former should be termed the "measure of ionisation" instead of the "ratio of dissociation" or the "measure of affinity." He objected to the use of the term "dissociation" on the ground that the ions supposed to be present were still held together somehow, so that they could not diffuse away from each other. He considered that the ions could not be independently mobile in the liquid, and that the *rôle* of the solvent is not merely to give the ions space to resolve themselves, for different solvents act differently towards the same substance. Van't Hoff's argument that osmotic pressure is due solely to the kinetic pressure of the molecules or ions does not necessitate the conclusion that the forces between these are small, but merely that the space within which they are bombarding is small compared with the space rate of variation of these forces. He regarded, however, the whole of Van't Hoff's argument as fallacious, for according to it one salt molecule could never produce osmotic pressure in its own neighbourhood by any forces of attraction between it and the solvent; this he considered to be erroneous, for if the semipermeable membrane were affected by the salt to a smaller degree than the water, there would be a difference of pressure in the solvent near and far from the salt, and this would act on the semipermeable membrane even though it were permeable to the solvent. He considered that there were other explanations preferable to that given by Van't Hoff. The mobility of the ions required by the laws of electrolysis is not greater than that required by osmotic pressure, and does not necessitate true dissociation. The continual interchange of atoms in contiguous molecules, which Williamson's and Clausius' theories alone require, is sufficient for this purpose, and such interchange may be effected by the formation of complex molecules followed by tautomerism. He considered it undoubted that solution is a true chemical combination. He thought that the energy required for dissociation might be supplied by assuming an affinity of the element for electricity, or supposing the ions to be allotropic atoms with different internal energy from that possessed by ordinary atoms; on the former assumption, however, the atom with its electrical charge combined would not be acted on by electrical forces required in the manner to explain electrolysis, and he thought that the facts of solution might be explained more simply by chemical combination than by the idea of allotropic atoms. He did not consider that the explanation offered by the dissociationists as to the heat of neutralisation explained anything. A rough calculation led to the estimate that an atom would acquire its ionic velocity in 10^{-15} of a second and 10^{-20} of a centimetre, in which case Ohm's law would not fail owing to the smallness of the intermolecular bombardment differences until the rate of the alternating current is comparable with that of light.

O. Lodge thought that the moment during which molecules are changing partners (a change proved by the existence of double decomposition) afforded an instant of potential dissociation sufficient to account for electrolysis; if, however, this instant were not long enough, we might fall back on the outlying atom stragglers of gross complex molecules without admitting that extreme state of dissociation which the physicists maintain. He had objected to Ostwald's experimont of producing electrolysis by an electrostatic charge on the ground that the experiment was an imaginary one (see Ostwald's remarks below), but even if it could be performed, the accepted laws of electrolysis would enable us to predict what would happen, the results being the same as if the current were derived from a battery.

W. Ostwald said that if a current from a battery is led into two beakers containing copper sulphate solution, connected by a siphon with its ends covered by a membrane, and filled with potassium ferrocyanide solution, a deposit of copper ferrocyanide is formed on the membrane, and through this no copper salt can pass; after a time, a deposit of metallic copper forms on the positive side of the membrane, showing that the latter is impermeable to the copper ions; these get filtered off, the electric charges with which they were combined alone pass through the membrane. K and Cl ions pass through a ferrocyanide membrane, Ba and FeC_6N_6 ions do not. In a salt which consists of one ion which can pass and one which cannot, such as barium chloride, the former passes to a certain extent, but is prevented from going far by the negative charge on it being attracted by the positive charge on the other ion which remains on the other side of the membrane. This explains why the ions cannot be separated by diffusion. The addition of an ion which can pass, such as K, to the barium chloride allows the chlorine of the latter to pass freely; but this might be due to previous double decomposition, potassium chloride being formed; but the free passage of the Cl ions may also be effected by placing other positive ions capable of passing on the *other* side of the membrane, as, for instance, copper nitrate; the Cl ions then pass freely in one direction and the NO_3 ions in the opposite direction: here no double decomposition is possible and the results can only be explained by free migrating ions. He considered that the energy required to dissociate a compound into its ions might be much less than that required to dissociate it into ordinary uncharged atoms. It was impossible to deny that the facts could be explained by theories other than Arrhenius' dissociation theory, but the latter is consistent with a very great number of facts. The experiment which Pickering and Lodge had referred to had actually been successfully performed, and no more involved the creation of energy than the production of a spark from bodies charged by induction. He considered that the opposition of chemists to the dissociation theory was merely a matter of feeling similar to that which led them for a time to oppose the idea of the dissociation of ammonium chloride by heat. The dissociation theory explains the difference between the behaviour of electrolytes and organic compounds as analytical reagents. The law of constant proportion is no argument against the theory, for the ions are charged with equal quantities of opposite electricities, and, for the solution to be electrically neutral, these electricities, and, consequently, the different ions, must be present in equivalent proportions. In answer to Armstrong, he pointed out that pure hydrochloric acid, like pure water, was a non-conductor, and the latter, like the former, would be a conductor in a suitable solvent: there was already some evidence that water was dissociated to a small extent.

J. Van't Hoff said that in dilute solutions a law corresponding with Avogadro's existed, and dissociation into ions was a necessary consequence of this. The action on the semipermeable membrane is due to the shock of the dissolved molecules and also to the difference of the forces acting on them (? on it) from the solvent on one side, and from the solution on the other. The result of the shock is directly proportional to the concentration, while that of the attraction is proportional to its square, so that the latter vanishes in dilute solutions, and the shock is alone the origin of pressure. Although these views are intended more to popularise than to prove the laws in question, Van der Waals' investigation of the kinetics of the action leads to a precisely similar result. According to his own theory, the depression of the freezing point is not independent of the nature of the solvent, and Raoult himself has abandoned his empirical constant in favour of Van't Hoff's formula.

W. N. Shaw took objection to some of the substances, such as the monohydrate of sulphuric acid, which Pickering quoted as solvents. He considered that a solvent could not be considered as inert if it caused the dissociation of the dissolved substance. He alluded to stannic chloride (*Phil. Mag.*, 1890, 383) as a substance which is converted into an electrolyte by the addition of alcohol or water, but not by the addition of chloroform or hydrogen sulphide, chemical action accompanying the change in the former case.

S. Pickering pointed out* that none of the positive arguments in favour of the existence of hydrates in solution had been refuted. There were difficulties in applying Kohlrausch's conductivity values for the calculation of the freezing points of sulphuric acid, and, even if we can correct the irregularities of the freezing points by the irregularities of the conductivities, this does not explain the existence of these irregularities; and their existence is inconsistent with any purely physical theory; moreover, non-electrolytes exhibit similar irregularities. The concordance exhibited by Arrhenius' calculations extended to 0·4° only, the total depression to 80°: an extension of the calculations to stronger solutions exhibits errors of different signs in different parts, and these finally attain a magnitude of 60°. Calculations on his own theory agreed with the observed values as far as a depression of at least 34°. Although Van't Hoff's equation represented the molecular depression to be independent of the nature or amount of the dissolved substance, yet both these affected it. The conservation of energy could not be said to be in open contradiction to the dissociation theory if sufficient hypotheses were made respecting the energy of the ions, yet these hypotheses themselves appeared to be in practical contradiction to the conservation of energy. They involve either the introduction of electric charges from nowhere capable of combining with matter to generate heat, or else they hypothecate a new form of atom which shall be *minus* that free energy which an ordinary atom possesses. S. U. P.

Deduction from the Gaseous Theory of Solution. By O. Masson (*Nature*, **43**, 345—349; *Zeit. physikal. Chem.*, **7**, 500—510).—In every simple solution the dissolved substance may be regarded as distributed throughout the whole bulk of the solution. Its total volume is therefore that of the solution, the solvent playing the part of so much space; and its specific volume is the volume of that quantity of the solution which contains 1 gram of the substance. To avoid confusion it is best to speak of this as the specific solution volume of the substance. It is obviously in inverse ratio to the concentration.

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* The whole of Pickering's answer appeared in the *Chemical News* only.

Imagine a soluble solid in contact with water at a fixed temperature. The substance exercises a certain osmotic pressure, in right of which it proceeds to dissolve. This pressure is analogous to the vapour pressure of a volatile substance in space, the space being here represented by the solvent; and the process of solution is analogous to that of vaporisation (Nernst, Abstr., 1890, 3). If there is enough water present, the whole of the solid will go into solution, just as the whole of a volatile substance will volatilise if the available space is sufficient. If the solvent is present in excess, the solution formed will be unsaturated, and the dissolved matter will be in a state comparable to that of an unsaturated vapour; but if there is not excess of the solvent present, a saturated solution will be obtained in presence of undissolved solid, just as we may have a saturated vapour in the presence of its own liquid or solid.

Suppose now that the temperature, in place of being fixed, is allowed to vary, a rise of temperature will disturb equilibrium, and its re-establishment would necessitate increased solution or vaporisation, as the case may be. In the case of a volatile liquid, it will become more volatile as the temperature rises, until when the critical temperature is reached it becomes infinitely volatile, and for higher temperatures can no longer exist in the presence of its own vapour, no matter how great the pressure may be. And from the analogy between solution and vaporisation, we may expect for every substance and its solvent a definite temperature, above which the substance cannot exist in presence of its own solution. This may be spoken of as the critical solution temperature.

The solution of a solid substance has here been compared to the vaporisation of a volatile liquid, but for purposes of a stricter analogy volatile solids, such as camphor or iodine, may be taken. A volatile solid will not reach its critical point without having first melted at some lower temperature, and a similar change should be exhibited in the solution process. At some definite temperature below that of infinite solubility, we may expect the solid to melt. This solution melting point will not be identical with, but lower than, the true melting point of the solid, owing to solution of the solvent in the liquid, which will take place in accordance with the rule of reciprocal solubility.

The above hypothesis demands that increase of solubility with rise of temperature shall be as general a law as increase of vapour pressure. It seems to demand some connection between the true melting points of salts and the rates of their increase of solubility, a relation established in a general way by Tilden and Shenstone (Abstr., 1884, 254). Further, whilst no case is known of a solid substance having as such infinite solubility in any simple solvent, several cases are known of liquids of infinite solubility, and also of solids which, after they have melted in presence of their own solutions, become at some higher temperature infinitely soluble. The observations of Alexéeff (Abstr., 1886, 847) more particularly show that two liquids become one homogeneous solution at a temperature which depends on the ratio of the original ingredients. There is one ratio which demands a higher temperature than any other; this is the critical solution temperature, above which either ingredient is infinitely soluble in the other.

From the observations of Alexéeff on the solubility of aniline in water and of water in aniline at different temperatures, the author deduces experimental evidence in favour of the above views. He also calculates the specific solution volumes of aniline in water at different temperatures, and plots the values against the temperature. The curve so obtained is strikingly similar to the curve given by Ramsay and Young for the specific volume of alcohol and its saturated vapour at different temperatures, thus affording additional support to the view that solution and vaporisation are perfectly analogous processes. H. C.

Deductions from the Gaseous Theory of Solution. By S. U. Pickering (*Nature*, **43**, 488).—When water crystallises from a solution by cooling, the tendency of the water molecules to coalesce will, on the hydrate theory, be partly counterbalanced by the attraction of the other substance present, so that the freezing point will be lower the more of the other substance, say salt, there is present. Similarly, the temperature of crystallisation of the salt from strong solutions must be lower the more water there is present. The curve formed by the latter temperatures gives what is generally termed the solubility of the salt in water, and the solubility is thus seen to increase with temperature. At a temperature above that of the solidifying point of the salt, no salt will be able to crystallise, and the solubility of it in water will be infinite; whilst at temperatures above the solidifying points of both salt and water, the mutual solubility of these will be infinite, and a homogeneous liquid will be produced. Similar results will be obtained if the two substances separate in the liquid, instead of the solid, condition, and hence the existence of a "critical solution temperature" may be deduced from the hydrate, as well as the gaseous, theory of solution (see preceding abstract). The author considers that the fact that osmotic pressure is numerically equivalent to what the gaseous pressure of the dissolved substance would be, does not prove that this substance is a gas when dissolved. The osmotic pressure has not yet been proved to be measured by $\frac{1}{2}mv^2$, and existing evidence is strongly opposed to the idea that the solvent only "plays the part of so much space." The only explanation yet offered by the supporters of the gaseous theory as to the cause of a solid dissolving at all is that it "exercises a certain pressure, in right of which it proceeds to dissolve," and the author calls on them to substantiate the existence of a pressure which has not yet been recognised. S. U. P.

Some Ideas about Solution. By W. Ramsay (*Zeit. physikal. Chem.*, **7**, 511—513).—The curves constructed by Masson (this vol., p. 791) for the specific solution volumes are isobaric curves. The data of Alexéeff are not sufficient to serve for the construction of the isothermal curves, but were it possible to determine the osmotic pressures of the different mixtures, isothermal curves could then be obtained analogous to those of Andrews and others for gases. Such solution isothermals should be similar in form to the isothermals for gases.

If we imagine the isothermal curve for solutions to be of similar form, say, to that of Andrews for carbonic anhydride, the continuous passage of gas to liquid in the latter case would be replaced by a continuous change from the one solvent to the other in the former. In that portion of the curve which represents the period of transition from gas to liquid, we may have represented certain labile conditions which it is possible to realise, such as that in which the gas exists at a pressure above that required for liquefaction, and that in which the liquid exists at a pressure below that under which vaporisation usually takes place. In the case of solutions, the first of these conditions would find its analogue in the phenomenon of supersaturation, as for example in the case noticed by Nicol, of the dissolution of anhydrous sodium sulphate in a saturated solution of the same salt. The second condition may perhaps correspond with that in which a syrup is formed, as when at high temperature water dissolves in cane-sugar, and the liquid on cooling remains viscid without crystallising.

The suggestion is also made of the possibility of determining the specific heats for constant osmotic pressure and for constant concentration, and of studying the isentropic relations in the case of solutions. H. C.

Solubility of some Substances in Mixtures of Water and Alcohol. By G. BODLÄNDER (*Zeit. physikal. Chem.*, **7**, 308—322).—Although many experimental data exist with reference to the influence on the solubility of a substance in water exercised by the presence of a third substance, no generalisations have up to the present been effected, with the exception of the laws which Nernst has shown (Abstr., 1890, 3) hold in the case of electrolytes. In accordance with Nernst's deductions, a third substance, if a non-electrolyte, should exercise no influence on the solubility, and should itself dissolve in an aqueous solution, just as in pure water. Hence the solubility of a substance in water should be in no way altered by the addition of alcohol to the water, provided that the substance itself is quite insoluble in alcohol.

Experiments on the solubility of a number of substances, both electrolytes and non-electrolytes, in mixtures of alcohol and water, prove, however, that this is not the case. If in 100 c.c. of the alcoholic solution there are contained S grams of dissolved substance, and W grams of water, and the alcohol exercises no influence on the solubility, the proportion of salt to water, S/W, should remain constant whatever variation takes place in the amount of alcohol present. But it was found in all cases, that as the amount of alcohol was increased, the ratio S/W decreased, so that water which contains alcohol in solution will not dissolve any third substance to the same extent as pure water, and the solubility will decrease as the amount of alcohol present increases.

Two assumptions may be made with reference to this behaviour.

A given amount of water may be able to dissolve only a certain amount of alcohol or of any other substance, but not the two together, so that if to a saturated solution of the one a quantity of the other be added, the water will be divided between the two, to the exclusion of a certain portion of the substance which it originally held in solution. Or, on the other hand, it might be that the addition of alcohol to water effected a decrease in its solvent action on other substances, comparable with the reduction which it effects in the freezing point. Both these assumptions, and the further deductions which they involve, are fully considered by the author, but neither appears to hold in the cases studied.

The only explanation remaining of the influence exercised by the alcohol is that it is a purely mechanical one, and simply due to the dilution of the water, and consequent distribution over a larger space. Theoretical considerations have led the author to the conclusion that if this is so in saturated solutions of a substance in water containing different amounts of alcohol, the ratio of the amount of water, W, to the cube root of the amount of the dissolved substance should be approximately constant. This relation is, as a matter of fact, found to hold experimentally in those instances which have been quoted above.

The experimental data given include the solubility of sugar, potassium and sodium chlorides and nitrates, and ammonium sulphate. In all these cases the ratio $W/\sqrt[3]{S}$ is approximately constant. With potassium chloride and nitrate and sodium nitrate, the values at first increase slightly with increasing amounts of alcohol, and then decrease, a behaviour which may be due to dissociative or associative changes. In the case of sodium chloride, a marked increase in the values of the ratio takes place throughout with increasing amounts of alcohol. But if the assumption is made of the existence of a hydrate, $NaCl,2H_2O$, and the results calculated on this basis, the values so obtained are perfectly similar in character to those with the other salts just mentioned. With ammonium sulphate, difficulties were experienced, owing to the separation of alcoholic solutions of this salt into layers (see Traube and Neuberg, Abstr., 1888, 783), but by considering the upper and lower layers in each case separately, normal results were obtained. H. C.

Solubility of Mixed Salts in Water. By G. BODLÄNDER (*Zeit. physikal. Chem.*, **7**, 358—367).—In a former paper (preceding abstract), the author studied the solubility of various substances in mixtures of water and alcohol, the compounds chosen being soluble in water, but insoluble in alcohol. He now investigates the effect produced on the solubility of one salt in water by the addition of another. The salts chosen were sodium nitrate and chloride, and potassium nitrate and chloride. The conditions of experiment differ from those of Nernst and Noyes (compare Abstr., 1890, 3; and this vol., p. 142) in so far as the above-mentioned salts are all easily soluble in water, and not merely slightly soluble. As in the case of the addition of alcohol, the addition of a second salt diminishes the solubility in such a way that the quotient of the quantity of water present in the solution by the cube root of the quantity of original salt is approximately constant. The numbers obtained when sodium chloride was added to sodium nitrate solution would appear to indicate that the chloride exists as $NaCl,2H_2O$. J. W.

Determination of Affinity Coefficients. By M. CONRAD and C. BRÜCKNER (*Zeit. physikal. Chem.*, 7, 274—282 and 283—305).—The first of these papers deals with the action of alkyl iodides on the sodium compounds of phenols and cresols. The methods of investigation have been described in former papers (compare Abstr., 1889, 931; 1890, 4, 327, and 1046). The action of methyl, ethyl, and propyl iodides on sodium phenoxide dissolved in ethyl and methyl alcohols was studied. The action takes place more rapidly in the former than in the latter solvent. As in former cases, methyl iodide is found to have the greatest, and propyl iodide the least, activity, that of ethyl iodide being intermediate. The action of methyl iodide only on the sodium compounds of the cresols was examined. The action is more rapid than in the case of the phenol compound. It is also most rapid with paracresol, and least with orthocresol, metacresol occupying exactly a mean position between the two.

In the second paper, the action of alkyl iodides on ethereal salts of acetoacetic acid and its derivatives in the presence of sodium ethoxide is considered. In this case also, methyl iodide is found to exceed the other alkyl iodides in activity. The action in the case of methyl acetoacetate is, on the other hand, slower than in that of the ethyl salt. If the affinity coefficient for ethyl acetoacetate be taken in each case as 100, those of the other ethereal salts will be:—

	Methyl iodide.	Ethyl iodide.	Propyl iodide.
Ethyl acetoacetate	100	100	100
Methyl acetoacetate	56·7	70·1	86·6
Ethyl methylacetoacetate	—	357	—
,, ethylacetoacetate	291	343	421
,, heptylacetoacetate	273	290	—
,, allylacetoacetate	174	197	—
,, benzylacetoacetate	—	159	—
,, benzoylacetoacetate	61·6	70	—

If potassium is substituted for sodium ethoxide, the action in the case of ethyl acetoacetate is found to be more rapid. Propyl bromide acts less rapidly than propyl iodide. H. C.

Rate of Decomposition and Stereochemistry of Chlorhydrins. By W. P. EVANS (*Zeit. physikal. Chem.*, 7, 337—357).—From the mode of formation of various chlorhydrins, the author assigns to them appropriate stereochemical formulæ. These formulæ fall into four classes when considered with respect to the distance between the summits of the carbon-tetrahedra occupied by the chlorine atom and the hydroxyl group. It is assumed that the reaction $Cl{\cdot}R''{\cdot}OH + KOH = R''O + KCl + H_2O$ will take place the more readily, the nearer the chlorine and the hydroxyl are to each other in the molecule. Corresponding to the stereochemical formulæ, then, the rates of decomposition of the chlorhydrins by potassium hydroxide solution should also be capable of being arranged in four groups. Measurements were made at different temperatures to test the validity of these considerations. The following table contains the coefficients of velocity found by the author :—

		24·5°.	34°.	43·6°.
1.	Trimethylethylene chlorhydrin....	1·93	5·00	9·40
	Dimethylethylene chlorhydrin	1·73	4·70	11·00
2.	α-Dichlorhydrin................	0·76	2·27	6·70
	β-Dichlorhydrin	0·32	0·54	0·96
	Methylethylene chlorhydrin	0·049	0·147	0·31
3.	Ethylene chlorhydrin............	0·0068	0·019	0·052
4.	Trimethylene chlorhydrin........	0·0000	0·000	0·000

The agreement with the deductions from the stereochemical formulæ is satisfactory. J. W.

Action of Water on Normal Salts of Amines of the Paraffins. By A. Colson (*Compt. rend.*, **112**, 619—622).—If a hydrochloride of an amine is dissociated by water, the acid, as Berthelot has shown, will form a stable combination with the water, whilst that portion of the base which is free from chemical affinities will dissolve in the liquid in the same manner as a gas, and will have a definite tension at a given temperature. If air is passed slowly through the solution, the air saturated with aqueous vapour will form a mass of gas in which the amine will have a tension proportional to its tension in the liquid.

Air was passed into solutions of equivalent quantities of diisobutylamine and triethylamine hydrochlorides respectively for six hours, and the acidity of the liquid was then determined. With solutions containing 1 gram-mol. per litre, the ratio of the loss of amine at 100° was diisobutylamine : triethylamine : : 25 : 13; at 56—58°, the loss was less than one-third of that at 100°, but the ratio was 7 : 3, or practically the same. The ratio of the loss from a solution containing 1 gram-mol. per litre to that from a solution of half the strength was as 1·4 : 1, and the ratio between $\frac{1}{2}$ gram-mol. and $\frac{1}{4}$ gram-mol. was likewise 1·4 : 1. It follows that the tension of dissociation diminishes considerably as the concentration of the liquid decreases. A very slight excess of acid prevents any sensible loss even after six hours at 100°. C. H. B.

Inorganic Chemistry.

Coefficients of Volatility for Aqueous Hydrochloric Acid. By R. B. WARDER (*Chem. News*, **63**, 17—18).—100 c.c. of hydrochloric acid of known strength was submitted to fractional distillation in a flask of 250 c.c. capacity, placed in a cylindrical air-bath, and covered with a conical hood of sheet copper heated in such a way as to keep the temperature of the upper part of the flask from 40—50° above the boiling point of the liquid. By this means the condensation of moisture upon the sides of the flask was prevented, and the distillate obtained really represented the vapour escaping from the surface of the boiling liquid. Successive portions of the distillate were collected in receivers, which in the case of strong acids contained 10 c.c. of water to absorb acid fumes. The several fractions, after weighing in well-stoppered vessels, were titrated against sodium hydroxide, or against centinormal silver solution after evaporating with excess of ammonia. The amount of water present in any fraction was determined by deducting the weight of the acid from the total weight of the fraction; and the weights of water and acid thus found in each fraction were subtracted successively from the water and acid taken to find the composition of the residue after removal of this fraction. The mean composition of the boiling liquid during the removal of each fraction was expressed in the form $H_2O + nHCl$, the composition of the distillate being $H_2O + n'HCl$ or $H_2O + vnHCl$. The coefficient v was then found by dividing n' by n. Four distillations gave 25 pairs of values (see original) which could not be all expressed by one equation. When dilute acid ($n = 0{\cdot}07$ to $0{\cdot}11$) was boiled rapidly (about 1 gram distilling over per minute), the results agreed with the equation $v = 445n^3$. When strong acid was boiled rapidly, the values of v were somewhat greater than would be indicated by the equation last given, and were approximately represented by $v = 3063n^4$. These two empirical curves, which occupy different parts of the field, are entirely consistent with each other, but must be regarded as a first approximation only of the function sought. When the dilute acid was boiled from 20 to 60 per cent. more slowly, the values of v were about 10 to 30 per cent. less than those indicated by the equation given, and it therefore appears that v is a function of the rate of boiling, as well as of the composition of the liquid.

G. T. M.

Is it Possible to Form Ozone by Lowering the Temperature of a Flame? Is there Ozone Near to a Flame? By L. ILOSVAY (*Bull. Soc. Chim.* [3], **4**, 707—714).—The author's statement that ozone is not formed during rapid combustion has been traversed by Loew (Abstr., 1890, 330) and Cundall (Proc., 1890, 26). Both these writers indicate methods of detecting ozone formed by flames, using the odour and taste of the ozone for the purpose. Considering these tests unsatisfactory, the author has re-examined the question. Repeating the experiments of Loew and Cundall, the products of combustion in the first case, and the air taken from around the flame in the second, have not been found (1) to give the odour of ozone, (2) to render thallous oxide paper brown, (3) to permanently decolorise a solution of sulphophenylazo-α-naphthylamine so that naphthylamine no longer restores the colour. It is concluded, therefore, that the experiments of these chemists were insufficient to prove the formation of ozone in the special cases given. After the gas used had been carefully deprived of sulphur compounds, in one experiment the reaction with thallous oxide paper was obtained in about seven hours, but in several others failed. A new series of experiments, made with special precautions to keep the temperature of the flame low and with the aid of a special collecting apparatus, yielded the thallous oxide reaction in about 4—5 minutes, and the other ozone reaction in 10—15 minutes. By this modified method, the methane flame gives less, the hydrogen and carbon monoxide flames more ozone than the flame of illuminating gas.

The relative amounts of nitrous acid and ozone formed by the flame depend (*a*) on the temperature of the latter, ozone formation being favoured by a low temperature; (*b*) possibly on its surface.

Experiments made with oxygen in place of air did not yield such good results; the author intends to repeat them.

It was found impossible to obtain the reactions of ozone by Cundall's method even after 10 to 12 hours; the nitrous acid reaction was, however, very characteristic.

The author maintains that the partial conversion of oxygen into ozone, obtained by blowing a current of air or oxygen on to a flame, does not contradict his statement that "ozone is not formed during rapid combustion."

The above results agree with those obtained by Dewar, who ozonised oxygen by causing it to pass over white-hot platinum, and also with the experiments of Elster and Geitel. It is concluded that combustion is not the source of the ozone of the air, as the conditions found to be essential for its production are absent in ordinary combustion. W. T.

Conversion of Sodium Pyrophosphite into Phosphite. By L. Amat (*Compt. rend.*, **112**, 614—616; compare this vol., p. 641).—The change is more rapid the more concentrated the solutions, but the effect of dilution becomes smaller and smaller as the concentration diminishes. With solutions so dilute that the concentration is without influence, the rate of change is proportional to the quantity of acid present. Nitric and hydrochloric acids exert the greatest effect, sulphuric acid somewhat less, and phosphorous acid still less, whilst acetic acid has only a very slight effect.

The change in presence of alkali is subject to similar laws, the rate of change at each instant being proportional not only to the quantity of pyrophosphite present in the solution but also to the quantity of free alkali. C. H. B.

New Form of Silicon. By H. N. Warren (*Chem. News*, **63**, 46).—A form of silicon, crystallising in perfect and well developed oblique octahedra, was obtained on subjecting potassium silicofluoride to an intense heat in contact with impure aluminium. On separating the graphitoïdal silicon thus formed by the aid of dilute acids, small quantities of the new variety were obtained. Larger yields were procured, with varying success, by introducing pieces of metallic aluminium, about the size of a walnut, into a clay crucible containing a mixture of 4 parts of potassium silicofluoride with 1 part of potassium carbonate and 2 parts of potassium chloride, in a state of fusion. After the violent action attending the introduction of the aluminium had subsided, the crucible was urged to whiteness for about 5 minutes; after cooling, a button containing 80 per cent. of silicon was obtained. This was placed in a plumbago crucible with 12 parts of aluminium and 2 parts of tin, and the whole covered with a layer of sodium silicate. The crucible was heated at the highest temperature obtainable for about 2 hours; after cooling the crucible and breaking the piece of aluminium contained therein, the new modification was obtained in large, perfect crystals, having a full metallic lustre and resembling the crystals of cast iron, which are sometimes seen on breaking a pig of that substance; it is infusible and insoluble in all acids except hydrofluoric. G. T. M.

Action of Hydrogen Iodide on Silicon Chloride. By A. Besson (*Compt. rend.*, **112**, 611—614).—Dry hydrogen iodide has no action on silicon chloride at the ordinary temperature, but at a high temperature products of partial substitution are obtained; the determining cause of the reaction being the difference between the heats of formation of hydrogen chloride and hydrogen iodide, and the partial dissociation of the latter at the temperature of the experiment. Hydrogen iodide mixed with vapour of silicon chloride is passed somewhat rapidly through a glass tube heated to redness; the product is agitated with mercury to remove free iodine, and is then fractionated.

Silicon iodochloride, $SiCl_3I$, is a colourless liquid which boils at 113—114°, and does not solidify, even at −60°. It is not affected by light alone, but when exposed to air it becomes brown from separation of iodine, and this change is accelerated by light. It fumes in the air, is decomposed by water, and combines with ammonia to form a white, amorphous solid, $2SiCl_3I,11NH_3$, which is also decomposed by water; it does not form a compound with hydrogen phosphide, even under pressure and at a low temperature. Silicon iodotrichloride can also be obtained by heating silicon chloride with iodine in a sealed tube at 200—250°.

Silicon diiododichloride is obtained only in small quantity; it boils at 172°, does not solidify even at −60°, and rapidly becomes brown, owing to separation of iodine. It fumes in the air, burns with liberation of iodine, and is decomposed by water; when dissolved in carbon tetrachloride, it combines with ammonia to form a white, amorphous solid, $SiCl_2I_2,5NH_3$, which is decomposed by water. The diiododichloride is also obtained by saturating the iodotrichloride with hydrogen iodide at −22°, and heating the solution for 24 hours in sealed tubes at 250°.

The *chlorotri-iodide*, $SiClI_3$, was obtained in very small quantity; it fumes in the air, rapidly becomes red, gives a combustible vapour, and combines with ammonia. It boils at about 220°, and when strongly cooled remains in superfusion, but on agitation forms a white solid which melts at about −30°. C. H. B.

Action of Heat on Carbonic Oxide. By BERTHELOT (*Compt. rend.*, **112**, 594—597).—Carefully purified and dried carbonic oxide, when heated in glass tubes at 500—550°, always yields a small quantity of carbonic anhydride, without any separation of carbon. The quantity of anhydride formed is practically the same as at high temperatures, but in the latter case there is separation of carbon. The formation of carbonic anhydride at 500—550° is probably accompanied by the formation of a suboxide, as, for example, $10CO = C_8O_6 + 2CO_2$ C. H. B.

Reaction of Carbonic Oxide. By BERTHELOT (*Compt. rend.*, **112**, 597).—Carbonic oxide reduces ammoniacal silver nitrate, the liquid becoming brown even in the cold; when heated, an abundant black precipitate separates. The reaction is very sensitive, and can be obtained with an aqueous solution of the gas; the presence of even a large quantity of air does not interfere with the reaction.

C. H. B.

Reduction of Oxygen Compounds by Magnesium. By C. WINKLER (*Ber.*, **24**, 873—899).—The author has examined the reducing action of magnesium, and of magnesium in the presence of hydrogen, on the elements of the fourth group, and gives a detailed account of the experiments. The following results were obtained:—

Carbon.—Magnesium burns at a red heat in carbonic anhydride to form amorphous carbon; when heated with carbonates, however, an explosive action takes place. The reduction is generally accompanied with the formation of magnesium carbide and carbon monoxide. Carbon monoxide at a higher temperature is reduced to carbon. The carbon so obtained always contains magnesium, even after prolonged treatment with hydrochloric acid. When the experiment is conducted in the presence of hydrogen, no compound of carbon and hydrogen is formed.

Silicon.—Magnesium and silicon have a decided tendency to combine chemically with one another. The two elements combine with a faint evolution of light when gently heated together. Silica, when heated with magnesium, is converted, with evolution of light and scattering of the mixture, into a mixed product. The product in the cooler parts of the tube has the bluish-grey colour of magnesium silicide, that in the hotter part of the tube the brown of amorphous silicon. When the product is mixed up and again heated, a mixture of silicon and magnesia is obtained. If excess of silica be employed, no magnesium silicide is produced, but only silicon. Silicates are also reduced by magnesium. Silicon is without action on silica at a high temperature. When the reduction was conducted in an atmosphere of hydrogen, no compound of silicon with hydrogen was obtained.

Titanium.—Titanic anhydride, when heated with magnesium, is not reduced to titanium, but titanium monoxide and magnesium titanate are produced. The latter is not capable of further reduction. With a limited quantity of magnesium, other oxides of titanium, together with magnesium titanate, are formed. Magnesium titanide is not obtained. A compound of titanium and hydrogen does not appear to exist.

Zirconium.—The reduction of zirconic anhydride by magnesium takes place at high temperatures with evolution of light, but is usually incomplete. If the experiment is performed in an atmosphere of hydrogen, the latter is rapidly absorbed with the formation of black *zirconium hydride*, ZrH_2. Zirconium hydride is inflammable, and is not attacked by acids. Magnesium zirconide could not be obtained.

Cerium.—Cerium dioxide is reduced at high temperatures by magnesium, according to the proportions of the latter, either to cerium or cerium sesquioxide, with evolution of light. Cerium monoxide and magnesium ceride do not appear to exist. When the reduction is effected in hydrogen, the latter is rapidly absorbed, and *cerium hydride*, CeH_2, is formed. Cerium hydride is inflammable, is brownish-red, and is decomposed by acids. Lanthanum behaves in the same way as cerium, which points to its being a quadrivalent element, and to having a position in the natural system of elements different from that usually assigned to it.

Thorium.—Thorium dioxide is reduced to thorium on heating it with magnesium. When the experiment is conducted in hydrogen, the latter is absorbed, and thorium hydride, ThH_2, is formed. A monoxide of thorium does not appear to exist.

Germanium.—The oxide is reduced to germanium with a violent report and scattering of the mass.

Tin.—The oxide is violently reduced to metal with evolution of light and explosion, resulting in the violent shattering of the tube.

Lead.—The oxide is reduced to metal with a violent explosion and evolution of light.

The author points out that, like carbon and silicon, all the other members of the *main* sub-group of quadrivalent elements are capable of forming compounds with hydrogen, with the exception of titanium. The existence of a hydrogen compound of lanthanum points to its having a different position in the system of elements, as stated above. The hydrogen compounds obtained correspond with the hydrocarbons C_nH_{2n}, and the authors think that there can be no doubt that compounds will be obtained from them corresponding with the derivatives of the hydrocarbons and so-called organic compounds.

E. C. R.

Rubidium Barium Dithionate. By G. Bodländer (*Chem. Zeit.*, **14**, 1140—1141).—While preparing rubidium dithionate from rubidium sulphate and barium dithionate, tufts of interlacing, very slender, white, hair-like needles were observed to separate, and when isolated by repeated recrystallisations, these crystals were found to suffer no loss of weight at 100°, but at higher temperatures an evolution of sulphurous anhydride and water occurred, leaving a residue of rubidium and barium sulphates. Analysis indicates the composition $(S_2O_6)_3BaRb_4 + H_2O$ for this substance. The crystals are doubly refracting, and show extinction parallel and at right angles to the long axis; they are more soluble in warm than in cold water, and readily from supersaturated solutions. The solubility is diminished by the presence of excess of the rubidium sulphate, but increased when the barium dithionate is present in excess; but the composition and the physical characters of the double salt remain unaltered under these circumstances. D. A. L.

Allotropic Silver. By M. C. Lea (*Amer. J. Sci.* [3], **41**, 179—190, and 259—267; *Phil. Mag.* [5], **31**, 238—250, and 320—329).—Gold-like allotropic silver (Abstr., 1890, 213) behaves in a characteristic manner with strong acids. Hydrochloric acid has no action on normal reduced silver, but when it is added to the allotropic silver some silver chloride is always formed, although the amount is small because of the immediate conversion of the silver into the ordinary form. If the acid is diluted with 50 vols. of water, this last change is much slower, and about one-third of the metal is converted into chloride. Even when the acid is diluted with 100 vols. of water, the metal is changed into the ordinary white form, whilst a considerable quantity is converted into chloride. Sulphuric acid diluted with 50 vols. of water has no action on ordinary silver, but converts the gold-like modification into the normal form, and dissolves a small quantity. Sulphuric acid mixed with 4 vols. of water, and allowed to cool, converts the gold-like form, in a few seconds, into the intermediate modification described below; if the acid is mixed with 2 vols. of water, and applied hot, the metal changes instantly into the normal light-grey form. The action of strong acids on allotropic silver is not accompanied by any evolution of gas. Oxalic, citric, and tartaric acids have no action on the moist precipitated allotropic silver, but dry films, on paper, are converted by the same solutions into the ordinary white metal. Ammonia dissolves a small quantity of allotropic silver, but does not change it into the ordinary form.

Gold-like silver behaves with potassium ferricyanide, ferric chloride, &c., in the same manner as ordinary silver, but is more active.

An intermediate gold-like modification, D, has a bright-yellow instead of a deep-yellow colour, is harder, and can be burnished, is not converted into the white form by shearing stress, and gives no colour reactions with potassium ferricyanide or ferric chloride, which only cause a slight deepening of the colour. It is obtained by heating films of the gold-like modification C, on glass or paper, at a temperature just below that at which the paper begins to carbonise. No similar change is produced by merely drying the gold-like variety.

If the precipitated gold-like variety is subjected to prolonged washing, it dries with a deep copper colour. The washing is accomplished much more easily if a 2 per cent. solution of sodium potassium tartrate is used instead of water, until the process is nearly finished. Silver tartrate and stannous nitrate yield gold, blue, and other modifications of silver, but the products always contained considerable quantities of tin. Similar results were obtained with silver citrate.

High-tension electricity changes gold-like silver C into ordinary white silver, even with a moderately powerful discharge. If several films on paper are put together, and held between the conductors, there is a transference of some of the silver from one sheet of paper to the next. The parts which have been affected by the discharge no longer give any colour reaction with potassium ferricyanide.

Dry films of gold-like silver on glass, change to the white form when heated. After 9 hours at 100°, the edges of the film have become white, whilst the centre is completely changed into the intermediate variety D; at 180°, conversion into the intermediate form is complete in 10 minutes; at 200°, the edges become white in 10 minutes, and the conversion into ordinary white silver is complete in half an hour.

The dried precipitate, in mass, undergoes a similar change at 180—190°. A film of gold-like silver on pure paper is converted into the intermediate form in half an hour, if immersed in water heated at 99—100°; a similar film on glass passes completely into the normal silver in 24 hours, without disintegration of the film.

The application of the slightest friction or shearing stress immediately changes the gold-like silver C, into white silver. If this change is partially produced by friction, and the substance is left at rest, the change spreads spontaneously through the whole mass. All solid specimens of allotropic silver change spontaneously into white silver, even in the dark. Films on paper or glass alter more slowly.

Gold-like silver on glass or paper seems unchanged on exposure to light, but reacts less readily with potassium ferricyanide, and after exposure to one or two days of summer sunshine it is completely converted into the intermediate form D. Exposure for several months is insufficient to change it into ordinary metallic silver. Exposed under glass in a printing frame, however, it changes into the white form, because the glass becomes much hotter than the films that are freely exposed, and the change is brought about by heat rather than by light.

Of all the reagents which give colour reactions with allotropic silver (Abstr., 1890, 335), the best are potassium ferricyanide in 5 or 10 per cent. solution, which gives brilliant purples, blues, brownish-reds, and browns, and ferric chloride, which gives rose-colour. The colours are those of thin films.

It seems probable that the gold-like, intermediate, and normal varieties represent respectively atomic, molecular, and polymerised forms of the metal. Light, high-tension electricity and shearing stress affect silver haloïds in much the same way as they affect the allotropic forms of the metal. Heat also affects silver bromide (on paper), and makes it reducible by the ferrous oxalate developer, the change being slow at 100°, and very rapid at 140°. Since, however, the paper is not quite dry, the result must be regarded as an effect of the simultaneous action of heat and moisture. When heated with water at 100° for 3 or 4 hours, silver chloride darkens without evolution of any gas, and the water acquires a slight alkaline reaction, doubtless because of its action on the glass. Silver bromide, under similar conditions, changes only from yellow to greenish-yellow, and, finally, to dirty grey.

Sulphuric acid diluted with 2 vols. of water has no visible effect on silver bromide paper, but in one case, after washing with water and treatment with ferrous oxalate, the part that had been touched with acid was whiter than the rest. If the paper, after treatment with acid, is well washed, treated with very dilute ammonia, again washed, and treated with ferrous oxalate, those parts which have been touched with the sulphuric acid appear as brown marks on a white ground.

Silver photochloride, which, beyond a certain point, undergoes no further change when exposed to light, the author regards as analogous to the intermediate allotropic silver D.

Since the silver haloïds are affected by the same agents as allotropic silver, and always in the same direction (that is, towards condensation), the author considers that silver probably exists in its haloïd salts in one of its allotropic forms. C. H. B.

New Method of Making Alloys. By W. HALLOCK (*Chem. News*, **63**, 17; compare Spring, Abstr., 1882, 921).—When the metals of which Wood's alloy is composed are filed to fine grains and intimately mixed in the ratio of 1 part of cadmium (m. p. 315°), 1 part of tin (m. p. 230°), 2 parts of lead (m. p. 325°), and 4 parts of bismuth (m. p. 267°), and the mixture is tightly packed in a glass tube heated at 98—100° in a water-bath, in the course of some hours (generally a day or two) a homogeneous, liquid globule of the alloy is formed.

On the same principle, lead and tin may be melted together at 190—200° by simply laying a piece of tin on a carefully cleaned strip of lead, and placing the whole in an air-bath kept at the required temperature. Sodium and potassium readily form a liquid alloy at ordinary temperatures, when freshly-cut surfaces of the metals are placed in contact.

The author is of opinion that the method of making alloys here described will prove to be of general application, and suggests the following law as being highly probable:—An alloy can be produced out of its original constituents without considerable pressure (Spring, *loc. cit.*), if the temperature be above the melting point of the alloy, even though it be far below the melting point of the most easily fusible constituent. G. T. M.

Atomic Weight of Copper. By T. W. RICHARDS (*Chem. News*, **63**, 20—23, 34—36, 43—44).—Cupric bromide was prepared by the action of a slight excess of pure bromine on pure copper in presence of water. After completion of the reaction, the excess of bromine was expelled, by gentle evaporation to dryness in a glass dish, the nearly normal cupric bromide dissolved in a small amount of water, and the solution filtered through asbestos contained in a perforated crucible. The filtrate was barely acidified with pure hydrobromic acid, and concentrated to the consistency of syrup, the containing vessel being left wholly undisturbed in a vacuum for 36 hours. On agitation and cooling with ice, the resulting, odourless, black, supersaturated solution immediately crystallised to a mass of brownish-green needles, which were collected on a perforated crucible, and washed three times with a very little water. The dilute solution of these crystals deposited only an insignificant amount of the insoluble, basic bromide when allowed to remain for more than a week, and was, undoubtedly, a pure solution of cupric bromide. In it the ratio of copper to bromine was determined in the following way:—The copper, in 50—60 grams of the solution, was deposited, electrolytically, in a platinum dish, previously coated inside with a thin film of copper, so that the external conditions, before and after the analysis, might be the same. Slightly more than half a gram of the metal was obtained in each case. In determining the bromine in fresh portions of the solution, not only was the resulting silver bromide weighed, but also the silver required to form it; and this last value was determined according to two distinct methods. In the first place, the amount of silver required for a given weight of the copper bromide was calculated, and somewhat less than this quantity was weighed out, converted into nitrate, and the cupric bromide cautiously added to the warm, dilute solution. The deficiency of silver was made up by titration with a solution containing 1 gram of silver to the litre (compare Cooke, *Proc. Amer. Acad. Arts Sci.*, **17**, 18). After noting this first value for the amount of silver required, a slight, known excess of the standard solution was added, and the silver bromide was washed and weighed. The excess of silver in the filtrate was determined by means of ammonium thiocyanate; solutions containing an equivalent amount of pure copper nitrate and small, known amounts of silver nitrate being used as a standard of colorimetric comparison. This second method of determining the amount of silver required to precipitate the bromine is not so accurate as the first, but is of value as a check.

Assuming the ratio Ag : Br = 108·00 : 80·007, the mean atomic weight of copper, as given by the eight final and most trustworthy determinations, = 63·645, with a maximum of 63·664, a minimum of 63·628, and a variation from the mean of ± 0·018. This value for the atomic weight is considerably higher than that until now accepted, but agrees closely with the numbers obtained by the author in his previous investigations (*Proc. Amer. Acad. Arts Sci.*, **23**, 180). If lower values for Ag are accepted, the following ratios are obtained:—Ag : Cu = 107·93 (O = 16) : 63·60; Ag : Cu = 107·675 (Clarke) : 63·45; Ag : Cu = 107·66 (Meyer and Seubert) : 63·44; Ag : Cu = 107·06 (O = 15·87) : 63·09. G. T. M.

Artificial Cryolite and the Dissociation of Aluminium Fluoride. By A. v. Asbóth (*Chem. Zeit.*, **14**, 868—869).—By fusing together sodium chloride, aluminium fluoride and zinc, and heating strongly for 15 minutes, or by adding aluminium fluoride to molten sodium chloride and fusing until the evolution of chlorine ceases, a mass is obtained which, on treatment with water, leaves a pink, insoluble, amorphous powder, containing cryolite, to the amount of 46·88 per cent. by the first method, in which case zinc and aluminium chlorides are also formed, and amounting to 42·52 per cent. by the second method, the rest of the powder consisting of alumina, aluminium fluoride, iron oxide, and sulphuric acid. The powder at a high temperature approaching fusion, becomes granular and white.

D. A. L.

Carburation of Iron by the Diamond. By F. OSMOND (*Compt. rend.*, **112**, 578—580).—Electrolytic iron, when heated in contact with diamonds at a temperature exceeding 1035°, but not exceeding 1065°, and, therefore, below the melting point of pure white iron (1085°), is attacked superficially, and carburated at those points where it is in contact with the diamonds. At a temperature of 1085—1125°, under the same conditions, the iron melts, the diamonds are dissolved, and a regulus of white cast iron is obtained. With a higher proportion of diamonds, some of the latter remain undissolved, but have been converted into a form resembling graphite, and have taken up a certain quantity of iron. The results show that the diamond, as such, cannot effect cementation : but in contact with iron it undergoes molecular change, and afterwards carburates the iron. The diffusion of the carbon into the iron is accompanied by a diffusion of iron into the altered diamond.

When cooled in hydrogen from 1200° to 600°, the diamond shows no abnormal development or absorption of heat. Graphite seems to show a retardation of cooling between 725° and 685° : and carbon from sugar shows a somewhat more marked retardation between the same temperatures. The variations are not much greater than the errors of observation, but it is noteworthy that the temperature, 725—685°, approaches closely to the temperature of the recalescence of steel : and this agreement can scarcely be a mere coincidence.

C. H. B.

Formation of Coloured "Lakes." By L. VIGNON (*Compt. rend.*, **112**, 580—582).—The heats of neutralisation of stannic acid and metastannic acid respectively by potassium hydroxide are in the ratio 32·7 : 2·3, and these numbers may be taken as measuring the relative energy of the acid functions in the two cases.

If the two acids are boiled with phenosafranine in presence of sodium sulphate and the precipitates are washed until the washings are colourless, it is found that stannic acid has formed an intensely red lake, whilst the metastannic acid has acquired only a very pale rose tint. With stannic acid, 74 per cent. of the safranine in the solution is precipitated, whilst with metastannic acid the quantity removed is too small to estimate. In this case, the absorption of a basic colouring matter is coincident with the existence of a strongly marked acid function in the absorbent.

C. H. B.

Bromonitro-compounds of Platinum. By M. VÈZES (*Compt. rend.*, **112**, 616—619).—When a concentrated solution of potassium platonitrite is gently heated with bromine, the compound $K_2Pt,4NO_2,Br_2$ is obtained as a bright-yellow powder, consisting of microscopic, yellow prisms which act strongly on polarised light. No gas is evolved in the formation of the compound, and it undergoes no loss of weight at 100—110°; it is an additive product from the platonitrite, and may be called *potassium platibromonitrite.* It is only slightly soluble in cold water, but more soluble in hot water, from which it crystallises in orange-yellow crystals, provided that it has not been heated too long above 80°.

If an aqueous solution of the platibromonitrite is heated for a long time at about 80°, nitrogen oxides are evolved and the liquid becomes red. When concentrated at a gentle heat, or in a dry vacuum, it deposits red, prismatic crystals of potassium platibromonitrosonitrite, $Pt,Br_3,NO,2NO_2,K_2$, which remains unaltered at 100—110°. It is much more soluble than the platibromonitrite, especially in hot water; by prolonged heating with water it is decomposed, with evolution of nitrogen oxides and formation of potassium platinobromide.

Hydrobromic acid acts more slowly on potassium platonitrite, and the product is a mixture of the platibromonitrite and the platibromonitrosonitrite, which can be separated by means of their different solubilities in water.

If potassium platinobromide, or one of the bromonitro-compounds, is heated with excess of potassium nitrite, the whole of the bromine is removed and the platonitrite is formed. The series of the bromonitro-compounds is, therefore, $K_2Pt,4NO_2$, $K_2Pt,4NO_2,Br_2$, $K_2Pt,NO,2NO_2,Br_3$, K_2PtBr_6.

The author was unable to obtain a compound, $PtBr_3,NO,K_2Br_2$, analogous to the nitrosoplatinochloride, $PtCl_3,NO,K_2Cl_2$. He has verified the composition of the salt $K_2Pt,4NO_2,Cl_2$, described by Blomstrand.

C. H. B.

Double Nitrites of Rhodium. By E. LEIDIÉ (*Bull. Soc. Chim.* [3], **4**, 809—814; see Abstr., 1890, 1382).—Claus and Lang have attributed contradictory properties to the double nitrites of the platinum metals, particularly to those of rhodium. Again, doubt is cast on Gibbs' method of separating these metals by means of the double nitrites, owing to the known inaccuracy of his statements concerning the solubility of the sulphides of the platinum metals in alkaline sulphides. To aid in the elucidation of the questions involved, the author has studied particularly the double nitrites of rhodium.

Contrary to the statements of Claus, there is but one potassium rhodium nitrite, $Rh_2(NO_2)_6,6KNO_2$. When prepared according to the method given in detail by the author, this salt forms white, microscopic crystals, without action on polarised light. It is almost insoluble in cold water, and insoluble in an excess of potassium nitrite, a 30 per cent. solution of potassium chloride, a 50 per cent. solution of potassium acetate, or in alcohol. Hot concentrated hydrochloric acid converts it into the double chloride, $Rh_2Cl_6,6KCl + 3H_2O$, obtained by Claus. This salt is very insoluble in water, which decomposes it into potassium chloride and the more stable chloride, $Rh_2Cl_6,4KCl$, the salt produced on mixing solutions of the two chlorides.

Sodium rhodium nitrite resembles the potassium salt in composition, and the method of preparation differs only in detail from that employed for the latter. It forms white, rather bulky, crystals, which act on polarised light. It is soluble in 2½ parts of water at 17°, and in an equal weight of boiling water, but is insoluble in alcohol. Hydrochloric acid readily attacks the sodium salt with the production of the double chloride, $Rh_2Cl_6,6NaCl + 18H_2O$.

The ammonium salt is prepared from the sodium rhodium nitrite by the addition of ammonium chloride.

Ammonium nitrite cannot be employed directly, on account of its ready decomposition by heat. In solubility and reactions, ammonium rhodium nitrite closely resembles the potassium salt.

Barium rhodium nitrite is prepared in much the same way as the potassium salt. It crystallises with 12 mols. H_2O, forming white, bulky crystals, which act on polarised light. The anhydrous salt is soluble in 50 times its weight of water at 16°, and in 6½ times its weight of boiling water. Hydrochloric acid converts it into a mixture of barium and rhodium chlorides, forming no definite double salt. The barium may be precipitated from the mixture by the calculated quantity of sulphuric acid, and the rhodium chloride in this manner obtained free from alkali chlorides.

The soluble double salts of rhodium and sodium or barium yield no precipitate with sodium hydroxide or carbonate, or with barium hydroxide, and give the insoluble double nitrites of potassium or ammonium with potassium hydroxide or carbonate, or ammonium carbonate or ammonia, respectively. Hydrogen sulphide or sodium sulphide precipitates rhodium sulphide slowly in the cold, more rapidly on heating to 100°. The properties of its double nitrites may be utilised for the extraction of rhodium, for its separation from other metals of the platinum group, and for its quantitative estimation.

W. T.

Organic Chemistry.

Halogen Derivatives of Amylene. By J. KONDAKOFF (*Ber.*, **24**, 929—933).—Hell and Wildermann, in a paper on the halogen derivatives of amylene (this vol., p. 533), state that for 60 years scarcely anything has been published on this subject. The author draws attention to the fact that since 1885 he has published a series of papers, in the *Journal of the Russian Chemical Society*, on this subject, and obtained the following results:—

Ordinary amylene consists (Flawitzky, Wischnegradsky, Eltekoff, &c.) of a mixture of isopentane with small quantities of trimethylethylene, unsymmetrical methylethylethylene, and propylethylene; according to Eltekoff, it consists of isopentane, trimethylethylene, unsymmetrical methylethylethylene, symmetrical methylethylethylene, and isopropylethylene. Both Gutrie and Bauer, and Hell and

Wildermann worked with this mixture. The author, however, employed amylenes of known constitution.

Trimethylethylene, treated with gaseous chlorine at +16° and −20°, gave the compounds C_5H_9Cl and $C_5H_{11}Cl$, and trimethylethylene chloride, $C_5H_{10}Cl$ (b. p. 133—135°). Besides these products, others, of higher boiling point, are obtained if excess of chlorine is employed, or if the trimethylethylene is cooled with calcium chloride and snow and treated with liquid chlorine. In the latter case, the action takes place with hissing and evolution of heat, and is very like the action of bromine. The product consists of $C_5H_{10}Cl_2$, $C_5H_9ClCl_2$, and $C_5H_8Cl_4$, together with an insignificant quantity of C_5H_9Cl and $C_5H_{11}Cl$.

Isopropylethylene, when treated with gaseous chlorine, yields almost entirely isopropylethylene chloride (b. p. 143—144·5°), and only a small quantity of α-ethylallyl chloride, $CH_2\colon CEt\cdot CH_2Cl$.

The mixed amylene, which consists chiefly of isopropylethylene and the unsymmetrical methylethylethylene, when treated with gaseous chlorine, gives isopropylethylene chloride and an unsaturated monochloride boiling at 102—103°, which is a derivative of methylethylethylene, and when warmed with potash yields an unsaturated primary alcohol. The latter consists of α-ethylallyl alcohol, $CH_2\colon CEt\cdot CH_2OH$, and probably $CH_2\colon CMe\cdot CH_2\cdot CH_2\cdot OH$.

With chlorine, symmetrical methylethylethylene yields, as chief product, methylethylene chloride, $CHMeCl\cdot CHCl\cdot CH_2Me$ (b. p. 138—139·5°), and a small quantity of the monochloride,

$$CHMeCl\cdot CH\colon CHMe.$$

The latter, on treatment with water, is converted into the corresponding unsaturated secondary alcohol, $OH\cdot CHMe\cdot CH\colon CHMe$, which boils at 117—118°; with bromine, it forms a viscous bromide, $C_5H_{10}Br_2O$; and by the action of mineral acids is converted into methylpropylketone.

The author is at present engaged in studying the action of chlorine on the residual hydrocarbons obtained by treating commercial amylene with sulphuric acid. He believes that the difference in the action of chlorine and bromine is only apparent, and is determined by the temperature and different conditions of aggregation of the two agents.

When dry gaseous bromine is passed over the mixed amylenes in an atmosphere of carbon dioxide at 20°, bromo-compounds are obtained, which were separated into the fractions (1) 80—110°, (2) 110—120°, (3) 120—180°. On treatment with water they gave dimethylethylcarbinol, the unsaturated α-ethylallyl alcohol which changes into the isomeric aldehyde, an unsaturated alcohol which changes into the ketone, a glycol boiling at 207—212°, and the bromhydrin of this glycol. If dry bromine is added to trimethylethylene, cooled with snow and salt, additive compounds are obtained without any visible evolution of hydrogen bromide. If the mixture is not cooled, heat is evolved, hydrogen bromide comes off, and the bromides C_5H_9Br and $C_5H_{10}Br_2$ are formed. The former of these compounds is converted into C_5H_9Br,Br_2 and then into $C_5H_8Br_2,Br_2$ by the further addition of bromine.

On the evidence of the above observations, the author expresses the chlorination of amylene by the formulæ (1) $C_5H_{10} + Cl_2 = C_5H_{10}Cl_2$, (2) $C_5H_{10}Cl_2 - HCl = C_5H_9Cl$, (3) $C_5H_{10} + HCl = C_5H_{11}Cl$.

Hence, those amylenes and generally olefines which combine easily with mineral acids yield unsaturated monochlorides; those which do not combine easily with mineral acids give additive products with chlorine. E. C. R.

The Complete Chlorination of Fatty Compounds of High Molecular Weight. By E. HARTMANN (*Ber.*, **24**, 1011—1026).—The chlorination was conducted in a similar manner for all the compounds. The method for caprylene is as follows:—Caprylene is treated with a rapid stream of dry chlorine, first in the cold and then at the temperature of the water-bath, as long as hydrogen chloride is formed. The product, which is a colourless oil, is freed from hydrogen chloride and free chlorine by means of an air-pump, transferred to tubes, and iodine added; the tubes are well cooled, and then antimony pentachloride is added. A vigorous action takes place. When this action is ended, the tubes are sealed up and heated at 70° for 3 hours, then opened, and again sealed and heated for 3 hours at 120°, 170°, and 200°. They are again opened, and the antimony pentachloride regenerated by passing in dry chlorine, and the tubes heated finally at 320°. The product is slowly poured into a mixture of concentrated hydrochloric acid and ice, and the oil which is precipitated treated with hydrochloric acid, and then with soda solution to get rid of the antimony and iodine. The product is next fractionally steam-distilled. The residue is heated with iodine and antimony pentachloride at 380°, and the product steam-distilled. The residue is finally crystallised from ether or light petroleum.

The following results were obtained:—Caprylene chlorinated at 320° gave perchloromethane, perchlorethane, perchloromesole, C_4Cl_6, and a brown compound, which, when further chlorinated at 380°, gave perchloromethane, perchlorethane, and perchlorobenzene.

Diisobutyl, chlorinated at 450°, gave perchloromethane, perchlorobenzene, and a trace of perchlorethane.

Diisoamyl at 360° gave about equal parts of perchloromethane, perchlorethane, and perchlorobenzene, and a trace of perchloromesole.

Cetyl iodide at 320° gave a large quantity of perchlorethane, together with some perchloromethane, perchloromesole, and a dark compound, which, on further chlorination at 360°, gave perchlorethane, perchlorobenzene, some perchloromethane, and a trace of a compound crystallising in small prisms and melting at 305·5°, which is probably perchlorodiphenyl.

Palmitic acid at 320° gave, as chief product, perchlorethane, together with a little perchloromethane and a dark compound, which, on further chlorination at 340°, gave, as chief product, perchlorethane and some perchloromethane and perchlorobenzene.

Pennsylvanian petroleum (commercial refined oil) at 350—360° gave perchlorethane and perchlorobenzene, small quantities of perchloromethane and perchloromesole, and a moderate quantity of residue, which, on chlorination at 450°, gave perchlorobenzene and perchloromethane. A specimen of petroleum boiling at 300—350° gave, on chlorination at a very high temperature, perchlorobenzene, as chief product, and perchloromethane.

Crude Galician ozokerite at 360° gave a large quantity of perchlorethane, together with perchloromethane, perchloromesole, perchlorobenzene, and a residue which on chlorination at 450° gave perchlorobenzene and a small quantity of perchloromethane. Ozokerite chlorinated at 450° gave perchloromethane and perchlorobenzene.

Bees'-wax at 450° gave a large quantity of perchloromethane, perchlorobenzene, and very little perchlorethane.

Perchloromesole, when heated for six hours at 450° with excess of antimony pentachloride containing iodine, is converted almost entirely into perchloromethane. Perchlorethane under similar conditions is also converted into perchloromethane.

Hence the hydrocarbons of the fatty series yield, as the final result of energetic chlorination, perchloromethane and perchlorobenzene, whilst perchlorethane and perchloromesole are obtained as intermediate products.

The author also describes the preparation of diisobutyl and diisoamyl from isobutyl bromide and isoamyl bromide respectively. The bromides are mixed with dry ether, excess of sodium wire added, and the mixture allowed to remain for a day. The yield of diisobutyl amounts to 50 per cent. of that required by theory; the yield of diisoamyl to over 90 per cent. This method is much cheaper than employing the iodides. E. C. R.

Formation of Nitriles on Oxidation with Nitric Acid. By C. Hell and C. Kitrosky (*Ber.*, **24**, 979—987).—When castor oil is oxidised with concentrated nitric acid, it yields a mixture of mono- and di-carboxylic fatty acids, and also various neutral compounds containing nitrogen, which are volatile with steam. Large quantities of capronitrile (b. p. 164—165°), considerable quantities of œnanthonitrile (b. p. 180—185°), and small quantities of caprylonitrile (b. p. 200—205°) and valeronitrile (b. p. 140—143°) can be isolated from this neutral oil by fractional distillation, and probably also butyronitrile (b. p. 120—130°), but the quantity of the last-named compound is so small that it was not characterised with certainty; the other nitriles were identified by converting them into the corresponding fatty acids.

Fatty acids, such as caproic and œnanthylic acids, or a mixture of the two, do not yield volatile nitriles on oxidation with concentrated nitric acid; œnanthaldehyde, on the other hand, yields about 1 per cent. of œnanthonitrile on treatment with nitric acid of sp. gr. 1·23 (3 parts).

Acetone gives about 1 to 1½ per cent. of its weight of hydrogen cyanide on oxidation with nitric acid, and methyl nonyl ketone yields octyl cyanide.

The above results may perhaps be explained by assuming that the nitric acid is reduced to ammonia, hydroxylamine, &c., and that condensation then takes place between the unchanged aldehyde or ketone and the reduction product; this view is, to a certain extent, borne out by the fact that considerable quantities of ammonia are actually formed in the reactions. F. S. K.

Origin of the Higher Alcohols contained in Commercial Spirits. By L. LINDET (*Compt. rend.*, **112**, 663—666).—Fermentation of sugar and of commercial "maltose" with a large quantity of yeast (80 per cent. of the sugar) yields a product containing a much smaller proportion of the higher alcohols than fermentation with a small quantity of the yeast (20 per cent. of the sugar). Acceleration of fermentation by addition of brewer's grains has a similar effect, the proportion of the higher alcohols being distinctly reduced. Previous experiments showed that the lower the temperature at which fermentation takes place, the lower the proportion of the higher alcohols, and the author considers that these results confirm the conclusions already published (this vol., p. 411). C. H. B.

Glucosoxime and Levulosoxime. By A. WOHL (*Ber.*, **24**, 993—996; compare Jacobi, this vol., p. 644).—*Glucosoxime* is deposited in crystals when an alcoholic solution of anhydrous glucose and hydroxylamine is kept for 6 to 8 days at the ordinary temperature; it crystallises in small, anhydrous needles, melts at 135°, and does not decompose on prolonged heating at 100°. *Levulosoxime* can be prepared in a similar manner, but it is obtained in the form of a syrup which crystallises on keeping over sulphuric acid; it melts at 118° and resembles glucosoxime in appearance.

Ordinary reagents produce no precipitation in a solution of either of these oximes, and both compounds, even in presence of excess of alkali, prevent the precipitation of ferric hydroxide from solutions of ferric salts. Glucosoxime reduces ammoniacal silver solutions almost immediately, even in the cold, but levulosoxime does so only on warming; both compounds are feebly lævo-rotatory. On evaporating almost to dryness a solution of glucosoxime with concentrated soda, and then dissolving the yellowish residue in water, a solution which gives the Prussian blue reaction for hydrogen cyanide is obtained; the oximes of galactose, mannose, and levulose show a like behaviour.

When glucosoxime is dissolved in acetic anhydride containing a trace of zinc chloride, an energetic reaction takes place; on cooling, and pouring the solution into water, a thick oil is precipitated. This oil is readily decomposed by dilute alkalis, even in the cold, yielding a solution which contains hydrogen cyanide; when boiled with very dilute sulphuric acid, it is gradually decomposed into hydrogen cyanide and a substance which combines with phenylhydrazine yielding a yellow, crystalline compound which is not glucosazone.

F. S. K.

A Red Sediment formed in a Raffinose Solution. By F. G. WIECHMANN (*Chem. News*, **63**, 5—7).—Whilst engaged in the isolation of raffinose from a low beet-sugar, the author obtained a small quantity of a substance having a bright-red colour. This substance contained iron, but was shown by spectroscopic examination not to be hæmatin; it is remarkably fluorescent, and is insoluble in all ordinary solvents except concentrated mineral acids. No information is given as to its nature. G. T. M.

Action of Nitric and Sulphuric Acids on Vegetable Fibre. By J. LIFSCHÜTZ (*Ber.*, **24**, 1186—1192).—Cellulose can be prepared in large quantities by the following process:—Fir-wood (1 part). free from bark, is cut into cubes 10—15 mm. in length, and heated at 45—50° with a mixture (10—15 parts) of concentrated sulphuric acid (1 vol.) and 25 to 30 per cent. nitric acid (3 vols.) for 14—16 hours; the light-yellow product is then separated from the warm solution, washed first with cold and then with hot water, and boiled with dilute soda until it is reduced to a pulp. The dark-brown liquid is run off and the pulp washed thoroughly with water (acidified with sulphuric acid if alkaline) until the washings are colourless. The cellulose obtained in this way is quite colourless, has a neutral reaction, and does not give the reactions of lignin; it is very strong and fibrous and contains 1·5—1·8 per cent. of ash, but is free from nitrocellulose; the yield is 38—41 per cent.

The acid liquid, separated from the cellulose, contains considerable quantities of oxalic acid, small quantities of fatty acids, and substances, such as cellulosesulphuric acid, which reduce Fehling's solution; it is used again four or five times for treating fresh quantities of wood, the only difference being that, in each operation the mixture is raised to a temperature about 5° higher than that employed in the previous one. The nitric acid is then completely used up, and the clear solution, if left for about 24 hours, deposits a considerable quantity of oxalic acid; this product is nearly pure, and can be obtained in a state of purity by recrystallising once from water. In such a series of operations, the yield of cellulose is 38—40 per cent., and that of the oxalic acid 29—30 per cent. of the weight of the dry wood employed. The acid liquors remaining after separating the crystalline oxalic acid in the last operation contain about 30—32 per cent. of sulphuric acid, 1·5—2·0 per cent. of oxalic acid, and small quantities of cellulosesulphuric acid; after adding the proper quantity of nitric acid and a little sulphuric acid if necessary, a mixture is obtained which can be again used for treating a fresh quantity of wood. F. S. K.

Action of Phosphorus Oxychloride on Ethereal Silicates and their Chloro-derivatives. By H. N. STOKES (*Ber.*, **24**, 933—936).—The action of phosphorus oxychloride on the trichlorhydrin of ethyl orthosilicate, $SiCl_3{\cdot}OEt$, was studied in the hope of obtaining silicon oxychloride, Si_2OCl_6. The reaction, however, takes place in quite a different way. When the trichlorhydrin is heated with excess of phosphorus oxychloride in a sealed tube for 2 hours at 180°, ethyl chloride, a white, amorphous compound, and silicon tetrachloride are formed. The white, amorphous compound is freed from excess of phosphorus oxychloride by heating at 150—200° in a stream of dry air. On analysis, it gave numbers corresponding with the formula $SiP_2O_6Cl_2$. It is extremely hygroscopic, easily and completely soluble in absolute alcohol, which proves the absence of free silicic acid, and is more soluble in water, but deposits silicic acid from the solution. On heating at 200°, phosphorus oxychloride is slowly evolved: at a red heat, phosphoric anhydride is given off, and a transparent glass remains, which contains lumps of silicic acid, and is probably the compound SiO_2,P_2O_5. The author concludes that this white, amorphous substance is the chloride of a silicophosphoric acid. Neither the acid itself nor any of its salts could be isolated, as it is decomposed by water. When silver nitrate is added to the cold aqueous solution acidified with nitric acid and the silver chloride filtered off, the clear filtrate on addition of ammonia, deposits silver pyrophosphate, silver orthophosphate, and finally silicic acid. Phosphorus pentachloride at 100° easily converts it into silicon tetrachloride and phosphorus oxychloride.

The action of phosphorus oxychloride on the mono- and di-chlorhydrin of ethyl orthosilicate takes place according to the following equations:—

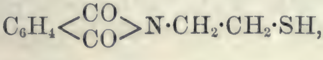
(1.) $2SiCl_2(OEt)_2 + 2POCl_3 = SiCl_4 + SiP_2O_6Cl_2 + 4EtCl$.
(2.) $4SiCl(OEt)_3 + 6POCl_3 = SiCl_4 + 3SiP_2O_6Cl_2 + 12EtCl$.

Ethyl orthosilicate is decomposed by phosphorus oxychloride according to the equation $Si(OEt)_4 + 2POCl_3 = SiP_2O_6Cl_2 + 4EtCl$.

Hexethyl disilicate, $Si_2O(OEt)_6$, is easily attacked by phosphorus oxychloride at 180°. Ethyl chloride is formed, together with a silicophosphoric chloride which is somewhat like the above, but has a different composition.

Ethyl disilicate chlorhydrin, when treated with phosphorus oxychloride, did not yield silicon oxychloride. E. C. R.

Derivatives of Ethylamine. By S. GABRIEL (*Ber.*, **24**, 1110—1121).—By the action of potassium hydrosulphide on bromethylphthalimide in alcoholic solution, the author has already found (Abstr., 1889, 870) that ethylmercaptophthalimide,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N\cdot CH_2\cdot CH_2\cdot SH,$$

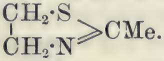
is formed. Further investigation has shown that the corresponding monosulphide is always simultaneously formed. To prepare ethylmercaptophthalimide in the pure condition, an alcoholic solution of bromethylphthalimide and potassium hydrosulphide is heated at 100° under pressure; the product, when poured into water, solidifies almost immediately to a crystalline mass, which is separated from the monosulphide simultaneously formed by conversion into the mercury or lead salt, preferably the latter, which is then decomposed by dilute sulphuric acid. Ethylmercaptophthalimide separates out on evaporating the filtrate, and is purified by recrystallisation from alcohol; it becomes plastic at 76°, melts at 79—80°, and is converted by boiling 20 per cent. hydrochloric acid into phthalic acid and *amidomercaptan hydrochloride*, $NH_2\cdot C_2H_4\cdot SH,HCl$, which crystallises in small, transparent needles.

Diphthalylamidoethyl sulphide, $(C_8H_4O_2{:}N\cdot C_2H_4)_2S$, is best obtained by heating bromethylphthalimide with a slight excess of alcoholic potassium sulphide in a reflux apparatus. Hydrogen sulphide is evolved, and after half an hour the product is poured into water; the yellow oil thus precipitated gradually solidifies, and, on recrystallisation from alcohol, is obtained in slender, flat needles melting at 128—129°. The mercaptophthalimide is obtained simultaneously in small quantity. The monosulphide is not formed by the action of potassium sulphide, K_2S, on bromethylphthalimide, but may be obtained by treating sodium ethylmercaptophthalimide with bromethylphthalimide; the yield is, however, not good.

To eliminate phthalic acid from the monosulphide, either hydrochloric acid or potash may be employed; the *thioëthylamine hydrochloride* thus obtained forms crystalline crusts or slender needles, melts at 131°, is hygroscopic and very soluble in water; its *aurochloride* forms yellow, radial, spherical aggregates, its *platinochloride* yellow needles, and its *picrate* acute plates melting at 212°. By the action of aqueous soda and benzoic chloride, it yields a *benzoyl* derivative, which crystallises in scales and melts at 107—108°. The free *thioethylamine*, $S\cdot(CH_2\cdot CH_2\cdot NH_2)_2$, obtained by the action of solid potash on a concentrated solution of the hydrochloride, is a colourless oil, boils at 231—232° under a pressure of 758 mm., and is miscible with water, forming a strongly alkaline solution.

When diphthalimidoethyl sulphide is oxidised with nitric acid of sp. gr. 1·25, nitrous fumes are evolved, and *diphthalimidoethyl sulphoxide*, $(C_8H_4O_2:N\cdot CH_2\cdot CH_2)_2SO$, is formed. The latter crystallises from alcohol or acetic acid in long, slender needles, melts at 189°, and is converted by hydrolysis with hydrochloric acid into *diamidoethyl sulphoxide hydrochloride*, $SO(CH_2\cdot CH_2\cdot NH_2)_2,2HCl$, phthalic acid, and other products. The former crystallises in long, slender needles.

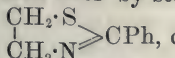
Under suitable conditions, ethylmercaptophthalimide may be oxidised to the corresponding bisulphide (see following abstract). The latter, on further oxidation with nitric acid of sp. gr. 1·25, yields *phthalyltaurine*, $C_8H_4O_2N\cdot C_2H_4\cdot SO_3H + 1\frac{1}{2}H_2O$. This forms compact crystals and has a bitter taste; it becomes plastic at 85°, and at 100° melts to a milky liquid, which is completely transparent at 102—103°.

Gabriel and Heymann have previously shown (Abstr., 1890, 524) that thiazolines may be prepared by the action of alkylene dibromides on thioamides, hydrogen bromide being eliminated. The reaction does not, however, succeed with thiacetamide. The author has now found a new method of preparing mesophenylthiazoline (see following abstract), and has also succeeded in preparing mesomethylthiazoline in a similar manner. For this purpose, dithioethylamine hydrochloride was boiled with anhydrous sodium acetate and acetic anhydride; after removing the excess of the latter, the syrup, which is almost certainly the *diacetyl* compound, $(NHAc\cdot C_2H_4\cdot S)_2$, was treated with phosphorus pentachloride, warmed for a few minutes, poured into water, the filtered solution made alkaline and distilled. The base comes over in the first portion, and is isolated by adding solid potash and extracting with ether. It boils at 144·5—145° under a pressure of 769 mm., and has the expected composition, C_4H_7NS. On oxidation with bromine-water, it yields taurine, and is converted by boiling hydrochloric acid into amidoethylamine hydrochloride and acetic acid; it must therefore be *mesomethylthiazoline*,  $\begin{matrix}CH_2{\cdot}S\\ |\\ CH_2{\cdot}N\end{matrix}\!\!>\!CMe$. Its *picrate*, $C_4H_7NS,C_6H_3N_3O_7$, forms long, flat needles melting at 169—170°, and the *platinochloride* a pale-yellow, crystalline powder readily soluble in water.

When bromethylphthalimide is heated by itself, it blackens and evolves hydrogen bromide. On further heating, a portion distils over from which phthalimide and ethylphthalimide were isolated, and a large quantity of carbon remains behind.

Bromethylamine hydrobromide acts on ethyl acetoacetate in presence of aqueous soda forming *ethyl bromethylamido-α-crotonate*, $C_2H_4Br{\cdot}NH{\cdot}CMe{:}CH{\cdot}COOEt$, which crystallises from light petroleum and melts at 48—50°. Bromethylphthalimide also combines with piperidine forming a syrup, which, on hydrolysis with hydrobromic acid and treatment with solid potash, yields 1-*amidoethylpiperidine*, $C_5NH_{10}{\cdot}C_2H_4{\cdot}NH_2$. It is a colourless liquid, boils at 183—184°, and absorbs carbonic anhydride from the air, forming crystalline crusts; it is miscible with water and has an odour resembling, but much weaker than, that of piperidine. Its *hydrobromide*, $C_7H_{16}N_22HBr$, crystallises from absolute alcohol in acute needles; the *aurochloride* forms long needles, and the *platinochloride* rhombic tablets. Its solution in hydrochloric acid gives a deep-red coloration with potassium bismuthoiodide.

H. G. C.

Dithioethylamine. By W. COBLENTZ and S. GABRIEL (*Ber.*, **24**, 1122—1125).—When the crude alcoholic solution of ethylmercaptophthalimide (see previous abstract) is treated with iodine or ferric chloride on the water-bath, it is converted into *diphthalylimidoethyl bisulphide*, $(C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2)_2S_2$, which crystallises in small plates melting at 138—139°. When heated with hydrochloric acid at 190—200°, it is hydrolysed with formation of *dithioethylamine hydrochloride*, $(NH_2{\cdot}C_2H_4)_2S_2,2HCl$. The latter melts at 203°, and, on treatment with benzoic chloride and aqueous soda, yields *dibenzamidodiethyl bisulphide*, $(NHBz{\cdot}C_2H_4)_2S_2$, which crystallises from hot alcohol in needles and melts at 132°. When heated with phosphorus pentachloride at 100°, it yields a pale-yellow syrup, which is dissolved in a small quantity of dry chloroform and mixed with benzene. The crystals which separate are collected, washed with benzene, and placed over sulphuric acid. They become moist and ball together in the air, and are decomposed by soda with formation of an oil which may be driven over by steam, and is identical with the mesophenylthiazoline  $\begin{matrix}CH_2{\cdot}S\\ |\\ CH_2{\cdot}N\end{matrix}\!\!>\!CPh$, described by Gabriel and Heymann (Abstr., 1890, 524). The above hygroscopic crystals gave on analysis numbers agreeing with the formula $(C_9H_9NS)_2,3HCl$, but the manner in which the reaction takes place is not yet fully ascertained.

H. G. C.

Action of Aqueous Ammonia on Isobutyl Chloride in Closed Vessels at 100°. By H. MALBOT (*Bull. Soc. Chim.* [3], **4**, 693—697).—The author has endeavoured to determine the best conditions for the production of isobutylamine. From the results of nine experiments carried out under different conditions, he concludes that:—(1.) It is not correct that an initial excess of ammonia always favours the formation of the primary amine to the exclusion of the secondary and tertiary products, but it considerably facilitates the transformation of the chloride. The rate of change of the isobutyl chloride augments very rapidly with the proportion of ammonia present. In two days, 31 per cent. is converted in the presence of two molecular proportions of ammonia, 50 per cent. with four; in three days 86 per cent. is transformed by six molecular proportions of ammonia, 95 per cent. by 10. Practically there is no advantage in using more than 10 molecular proportions of ammonia to one of isobutyl chloride.

(2.) Hofmann's hypothesis as to the formation of amines is inadequate to explain the results of these experiments, whereas the views put forward by the author in a previous paper (*Ann. Chim. Phys.*, March, 1888) account very well for the observed facts. W. T.

Hexamethylenamine. By Y. SCHWARTZ (*Chem. Zeit.*, **14**, 787).—*Hexamethylenamine tetrasilver bromide*, $C_6H_{12}N_4,4AgBr$, is formed when an ammoniacal solution of silver nitrate is mixed with an ammoniacal formaldehyde solution containing ammonium bromide; as also when hexamethylenamine itself is used, and when metallic bromides act on hexamethylenamine silver nitrate. It is a curdy precipitate which partly dissolves, the other portion becoming rapidly crystalline. When heated strongly, hexamethylenamine passes off, leaving a mixture of silver bromide, metallic silver, and some charcoal. Nitric acid rapidly oxidises it, yielding pure silver bromide. The compound resembles the hexamethylenamine derivatives described by Horton (Abstr., 1888, 1051). D. A. L.

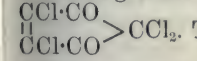
Essential Oil of Mustard. By P. BIRKENWALD (*Chem. Centr.*, 1891, i, 266—267; from *Pharm. Zeit. Russ.*, **29**, 785—787).—*Copper Compound of Allyl Thiocarbimide.*—A greenish-yellow, amorphous powder was found in the copper condenser when preparing allyl thiocarbimide. After washing it with alcohol, the colour changes to yellow; it dissolves in hydrochloric acid with evolution of hydrogen sulphide; it reacts with concentrated nitric acid, a strong odour of allyl thiocarbimide being emitted; it is blackened by potash, and allyl isothiocyanate is set free. The analysis agreed with a compound $CuS + C_3H_5NCS$.

Potassium Myronate.—The author has prepared potassium myronate from the seeds of *Brassica nigra* and *Sinapis junea* by Will and Körner's method; both the specimens melted at 135°, and decomposed at 145°. The loss on heating at 100° during four hours amounted to 2·43 per cent. in the case of the specimen from *Brassica nigra*, and to 3·32 per cent. in that of the specimen from *Sinapis junea.* The loss on heating should have been 4·3 per cent. to correspond with 1 mol. H_2O. The analysis of the specimen from *Sinapis junea* gave results corresponding with those which Will obtained with a specimen from *Brassica nigra.* J. W. L.

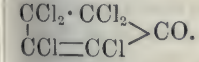
Investigation of Crude Acetone. By L. WOLFES (*Chem. Zeit.*, **14**, 1141—1142).—By fractionation, the crude oil boiling between 75° and 135° was separated into three fractions. From the first fraction, a substance boiling at 80° was obtained, which appeared to be methyl ethyl ketone. The second fraction yielded a substance boiling at 102—103°, which proved to be methyl propyl ketone; the absence of diethyl ketone was established. The third fraction, by repeated fractionation, yielded fractions of nearly equal amount; one boiling at 128—129° gave numbers between those required for methyl butyl ketone and allylacetone, the former substance being subsequently separated from its associates by means of sodium hydrogen sulphite. The oils not precipitated by this reagent were distilled from strong sodium hydroxide, and the indefinite substance (b. p. 128—130°) obtained was oxidised with nitric acid, evaporated to dryness, dissolved in water, and treated with barium hydroxide; the precipitate was found to contain succinic acid, the solution pyrotartaric acid. From the presence of the latter, the author infers that there is a ketone present containing a closed chain, probably identical with Kane's dumasin (*Annalen*, **110**, 21). D. A. L.

The Behaviour of Hexachlororthodiketohexene on Heating and towards Phosphorus Pentachloride. By T. ZINCKE and F. KÜSTER (*Ber.*, **24**, 924—928).—Hexachlororthodiketohexene was prepared in a dry state by distillation under reduced pressure. The hydrate cannot be used in these experiments. The hexachlorodiketone when free from water forms a thick red oil, boils at 199° under 60 mm. pressure, solidifies when kept for some time, and absorbs water from the air with production of the hydrate. The red colour appears to be due to a little tetrachlororthoquinone.

When heated in a tube at 300—310° for some hours, colourless needles are obtained, mixed with liquid products. The needles are perchlorobenzene (m. p. 224°). The liquid also contains perchlorobenzene, which is separated by adding light petroleum. The filtrate, on remaining some time, deposits crystals of $\gamma:\gamma$-hexachloroketopentene



$\left.\begin{array}{l}CCl\cdot CO\\ \parallel\\ CCl\cdot CO\end{array}\right>CCl_2$. The non-crystallisable product contains the $\beta:\gamma$-ketone,



$\left.\begin{array}{l}CCl_2\cdot CCl_2\\ |\\ CCl{=}CCl\end{array}\right>CO$.

When the diketone is heated with phosphorus pentachloride (2 mols.) at 250°, it is completely converted into perchlorobenzene. When the reaction takes place at 200—210°, some perchlorobenzene is formed, together with a compound containing phosphorus. The compound obtained from the latter, after treatment with water, melts at 203°, forms shining plates, and is soluble in ether. As this compound was only obtained in small quantities from the diketone, which latter is difficult to prepare in the dry state, the authors attempted to prepare it from tetrachlororthoquinone.

Orthoquinone was heated with phosphorus pentachloride (2 mols.) for half an hour at 200—210°. On treatment with water, a mass of shining plates was obtained. The perchlorobenzene was extracted from this with benzene, and the residue dissolved in ether and precipitated with benzene. Analysis showed that the compound was $C_6Cl_5 \cdot O \cdot PO(OH)_2$. It forms white, silvery plates, melts at 203° with blackening, is soluble in ether, somewhat soluble in water, and is reprecipitated by hydrochloric acid, and dissolves in soda without decomposition. It is identical with the compound obtained from hexachlordiketohexene, and is also obtained from the para-derivatives $C_6Cl_6O_2$ and $C_6Cl_4O_2$. It is an intermediate compound in the production of perchlorobenzene. E. C. R.

Derivatives of Palmitic Acid. By C. HELL and C. JORDANOFF (*Ber.*, **24**, 936—943).—The authors find that the most convenient material for the preparation of pure palmitic acid is Japanese wax, which yields one-half its weight of pure palmitic acid, whilst palm oil yields only one-fifth its weight. The acid was purified by distillation under reduced pressure, and melts at 62°.

α-Bromopalmitic acid is obtained by heating palmitic acid (175 grams) with phosphorus (7·1 grams) and bromine (65 c.c.). The product is purified by washing with water, when an emulsion is formed from which the acid is extracted with light petroleum. It crystallises in shining scales, melts at 51·5—52°, and solidifies in beautiful prisms or pyramids. It is insoluble, and when pure is incapable of forming an emulsion with water, dissolves easily in alcohol, benzene, ether, light petroleum, carbon bisulphide, and chloroform, and has no caustic action on the skin. The *ethyl* salt is obtained by passing hydrogen chloride into an alcoholic solution of the pure acid. It is a pale-yellow, fruity-smelling liquid, and boils at 241·5° under 38 mm. with slight decomposition.

α-Hydroxypalmitic acid is obtained by boiling the bromo-derivative with a slight excess of potassium hydroxide. When gently warmed with water, it forms an emulsion, and on raising the temperature of the water, rises to the surface as a yellow, transparent, gelatinous mass, which solidifies on cooling. It crystallises from alcohol in small, shining crystals, melts at 82—83°, and is easily soluble in alcohol, ether, and other organic solvents. The *copper* salt is obtained as a green precipitate on adding a hot alcoholic solution of copper acetate to an alcoholic solution of the free acid. The *lead* salt is obtained in a similar way as a white, powdery precipitate. The *barium* salt is obtained in crystalline flocks on adding barium chloride to an alcoholic solution of the ammonium salt. The *acetate*, $C_{16}H_{31}O_3Ac$, is obtained by boiling the acid with excess of acetic chloride, washing with water, and dissolving the oily product in ether. On distilling off the ether, it is obtained as a resinous mass. It crystallises from alcohol in white scales, melts at 62·5°, and is easily soluble in ether, less soluble in alcohol and other organic solvents.

α-Amidopalmitic acid is obtained by heating α-bromopalmitic acid with excess of alcoholic ammonia in a sealed tube for some hours on the water-bath. The product is mixed with water and acidified with sulphuric acid. A better yield is obtained by heating the mixture at 130—140°, and evaporating off the excess of ammonia and alcohol. It is a white, crystalline powder, insoluble in alcohol, ether, and benzene, sparingly soluble in cold acetic acid, and easily soluble in hot acetic acid, and dissolves easily in alcoholic alkaline hydroxides, from which solution the alkali salt crystallises in beautiful plates of fatty lustre. The *acetyl* derivative is obtained by boiling with excess of acetic chloride as a thick oil, dissolves easily in ether and alcohol, and has not been obtained crystalline.

α-Anilidopalmitic acid is obtained by boiling bromopalmitic acid with excess of aniline. From boiling alcohol, it separates as a powdery precipitate, melts at 141—142°, and is easily soluble in benzene and ether. It has not been obtained crystalline.

Palmitanilide is obtained by boiling palmitic acid with excess of aniline for about five hours, and washing the product with dilute acid and water. It distils at 282—284° under 17 mm. pressure without decomposition, and is so obtained as a colourless liquid, which solidifies on cooling to a crystalline mass. It crystallises from alcohol in long, soft, shining needles, melts at 90·5°, and is easily soluble in alcohol, more soluble in ether, benzene, and carbon bisulphide.

E. C. R.

Cyanopalmitic Acid, Tetradecylmalonamic Acid, and Tetradecylmalonic Acid. By C. HELL and C. JORDANOFF (*Ber.*, **24**, 987—993).—*Cyanopalmitic acid*, $C_{17}H_{31}NO_2$, is obtained when ethyl bromopalmitate is boiled for 4 to 5 days with potassium cyanide in alcoholic solution. The filtered solution is evaporated, the residue extracted with ether, the acid precipitated from the residual alkaline solution with hydrochloric acid, extracted by shaking with ether, and separated from regenerated palmitic acid by fractional crystallisation from light petroleum. It crystallises from hot glacial acetic acid in almost colourless plates, melts at 75—76°, and is moderately easily soluble in light petroleum; when heated at 220°, it is completely converted into palmitonitrile with evolution of carbonic anhydride, and when boiled with alcoholic potash, it yields palmitic acid.

Tetradecylmalonamic acid, $C_{14}H_{29}\cdot CH(CO\cdot NH_2)\cdot COOH$, is formed when cyanopalmitic acid is boiled with concentrated alcoholic soda for about two days. It crystallises from hot alcohol in nacreous plates, is insoluble in water and ether, and decomposes at 130—140° with evolution of carbonic anhydride, but without melting, being converted into palmitamide (m. p. 104—105°).

Tetradecylmalonic acid, $C_{17}H_{32}O_4$, can be prepared by boiling the preceding compound for a long time with alcoholic potash; it is a semi-crystalline powder, melts at 117—118°, and is readily soluble in hot alcohol and boiling acetic acid, but only very sparingly in ether, and insoluble in water. When heated at 150—170°, it is converted into palmitic acid. The *silver* salt, $C_{17}H_{30}O_4Ag_2$, is colourless; the *calcium* salt, $C_{17}H_{30}O_4Ca$, *zinc* salt, $C_{17}H_{30}O_4Zn$, and *cadmium* salt, $C_{17}H_{30}O_4Cd$, are crystalline; the *copper* salt, $C_{17}H_{30}O_4Cu$, decomposes at 180°.

F. S. K.

Propylideneacetic Acid from Malonic Acid and from Orthamidophenol. By T. ZINCKE and F. KÜSTER (*Ber.*, **24**, 908—911).—The authors undertook this work with the object of determining whether the acid $C_5H_8O_2$, obtained by them from catechol, was propylideneacetic acid, $CH_3\cdot CH_2\cdot CH\colon CH\cdot COOH$, or was identical with the ethylidenepropionic acid, $CH_3\cdot CH\colon CH\cdot CH_2\cdot COOH$, obtained from acetaldehyde and succinic acid. The solution of this question was of interest, because the authors had based the constitution of the hexachlorodiketone and other chloro-compounds obtained from catechol on the production of propylideneacetic acid. Ethylidenepropionic and propylideneacetic acids are easily distinguished by treating the acid with hydrogen bromide and boiling the resulting compound with water. If valerolactone is formed, then the compound is ethylidenepropionic acid. The authors find that the acid obtained from malonic acid and that from catechol behave alike. From both, a minute quantity of valerolactone was obtained, but the main product is an acid not containing bromine, which is probably an hydroxy-acid. The formation of a small quantity of valerolactone is probably due to a small quantity of the propylideneacetic acid having undergone molecular change.

Propylideneacetic acid was prepared from malonic acid according to the directions of Fittig and Fränkel. It boiled at 193—196°. The acid (4—5 grams), cooled with ice, was treated with somewhat more than an equal volume of hydrobromic acid saturated at 0°, and the mixture allowed to remain for a few days at the ordinary temperature, ice-cold water added, and the bromovaleric acid washed with ice-cold water and dried over potash and sulphuric acid. The bromovaleric acid was then boiled with water for some hours, the solution saturated with soda, and extracted with ether. On distillation of the product, 2—3 drops of valerolactone (b. p. 201·5—202°) were obtained. The main product of the action was not examined.

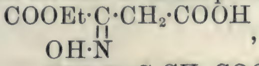
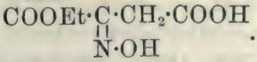
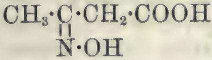
Propylideneacetic acid from orthamidophenol boiled at 192—195°. It was treated in the same way as the above acid, and yielded only a few drops of valerolactone. E. C. R.

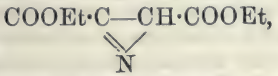
Velocity of Lactone-formation in the Case of various Hydroxy-acids. By E. HJELT (*Ber.*, **24**, 1236—1239).—The author has made a number of experiments on the relative velocity of the lactone formation in the case of the five hydroxy-acids named below. A solution of the pure lactone (0·0055 molecule in grams) is warmed with a slight excess of one-fifth normal potash, then cooled, exactly neutralised with hydrochloric acid, mixed with decinormal hydrochloric acid (50 c.c.), and diluted to 100 c.c. with water. The one-twentieth normal solution prepared in this way contains, besides the hydroxy-acid, potassium chloride and a small quantity of salt of the hydroxy-acid; the presence of the latter retards lactone-formation, but as the quantity is the same in all cases the values obtained are comparable one with another; the potassium chloride has no appreciable influence on the reaction. The prepared solutions are then heated at 100° in portions of 10 c.c., and after five minutes warming the initial condition is determined; portions of the solutions are taken after certain periods of time, poured into ice-cold water, and the acid present titrated with a centinormal solution of barium hydroxide.

The details of the results and the reaction coefficients calculated therefrom are given in a table. The times required for the conversion of 50 per cent. of the various acids into the corresponding lactones were found to be as follows:—Hydroxybutyric acid, 906 minutes; hydroxyvaleric acid, 126 minutes; hydroxycaproic acid, 70 minutes; hydroxyisocaproic acid, 56 minutes; hydroxymethylbenzoic acid, 15 minutes. F. S. K.

Isomerism of Oximes. By A. HANTZSCH (*Ber.*, **24**, 1192—1198).—Minunni's explanation of the isomerism of oximes (*Gazzetta*, **21**, 113) is a very improbable, if not an impossible, one, for various reasons. In the first place the iso- or β-oximes do not show the characteristic properties of partially reduced benzene derivatives, as they should if Minunni's formulæ were correct. Secondly, the formation of nitriles from β-aldoximes is quite inexplicable assuming Minunni's views to be correct. Thirdly, the intramolecular change observed by Beckmann in the case of the isomeric ketoximes cannot be explained in accordance with Minunni's formulæ. Fourthly, the number of isomerides actually capable of existence as proved by experiment, is not the same as the number required by Minunni's theory. The existence of isomeric oximes belonging to the fatty series is also a conclusive proof that Minunni's explanation of isomerism in the aromatic series is not the correct one.

The author then goes on to discuss the question of the isomerism of oximes of the fatty series, especially with regard to the results obtained by Cramer (compare following abstract). F. S. K.

Monoximes of Succinic Acid. By C. CRAMER (*Ber.*, **24**, 1198—1214).—The author's experiments have shown that the ethyl hydrogen oximidosuccinate obtained by Ebert from ethyl succinosuccinate and nitrous acid (Abstr., 1885, 1122) is stereochemically isomeric with the compound prepared by Piutti from ethyl oxalacetate and hydroxylamine (compare Abstr., 1889, 383 and 1890, 1239). The former is most probably the labile α-oxime of the configuration  $\begin{array}{l}\mathrm{COOEt\cdot \underset{\|}{C}\cdot CH_2\cdot COOH}\\ \mathrm{\quad OH\cdot N}\end{array}$, the latter the stable β-oxime of the configuration  $\begin{array}{l}\mathrm{COOEt\cdot \underset{\|}{C}\cdot CH_2\cdot COOH}\\ \mathrm{\qquad\quad N\cdot OH}\end{array}$. That this view is the correct one is rendered highly probable by the fact that the β-derivative exhibits analogy with the oxime of acetoacetic acid, which has doubtless the configuration  $\begin{array}{l}\mathrm{CH_3\cdot \underset{\|}{C}\cdot CH_2\cdot COOH}\\ \mathrm{\quad\; N\cdot OH}\end{array}$. The behaviour of the two compounds is also in harmony with this view; the β-dicarboxylic acid described below, which is obtained from the β-oximido-derivative, is readily converted into cyanoacetic acid, and the corresponding ethyl salt readily changes into ethyl nitrilosuccinate,

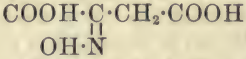


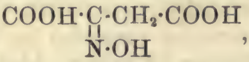
$$\begin{array}{c}\mathrm{COOEt\cdot C{-}CH\cdot COOEt,}\\ \diagdown\!\diagup\\ \mathrm{N}\end{array}$$

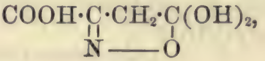
whereas the ethyl hydrogen salt of the α-derivative is readily decomposed into ethyl oximidopropionate and carbonic anhydride; these reactions are most easily explained by assuming the compounds to have the configurations assigned to them above.

Ethyl hydrogen α-oximidosuccinate, prepared as described by Ebert (*loc. cit.*), melts at 107°, and gives with ferric chloride a brown or a yellow coloration, according as the solution is concentrated or dilute; when heated at its melting point, or when warmed with water at about 80°, it is decomposed into ethyl β-oximidopropionate and carbonic anhydride.

Ethyl hydrogen β-oximidosuccinate (compare Piutti, *loc. cit.*) is most conveniently prepared by adding concentrated soda (1 mol.) to ethyl oxalacetate in the cold, and warming the sodium compound obtained in this way with a solution of a slight excess of the theoretical quantity of hydroxylamine hydrochloride, when the oxime is deposited as a colourless oil; soda (1 mol.) is then added, and, after keeping for several hours, the solution is strongly acidified, and the product extracted with ether. It melts at 54°, is more sparingly soluble than the α-compound, and gives an intense violet coloration with ferric chloride; under certain conditions, it undergoes decomposition into ethyl α-oximidopropionate and carbonic anhydride, but the change takes place far less readily than in the case of the α-compound.

α-Oximidosuccinic acid,  $\mathrm{COOH{\cdot}\underset{\substack{\| \\ OH\cdot N}}{C}{\cdot}CH_2{\cdot}COOH}$, prepared by hydrolysing the ethyl hydrogen salt with alcoholic soda (compare Ebert, *loc. cit.*), melts at 125°, being decomposed into water, carbonic anhydride, and cyanoacetic acid; the same decomposition takes place on heating an aqueous solution of the acid at 105—130°. In concentrated solutions, ferric chloride produces a brown, in dilute solutions a yellow, coloration.

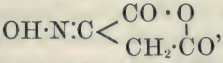
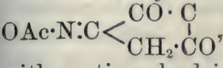
β-Oximidosuccinic acid,  $\mathrm{COOH{\cdot}\underset{\substack{\| \\ N\cdot OH}}{C}{\cdot}CH_2{\cdot}COOH}$, or



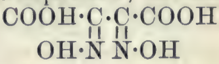
$$\mathrm{COOH{\cdot}\underset{\substack{\| \\ N}}{C}{\cdot}CH_2{\cdot}\underset{\substack{| \\ O}}{C}(OH)_2},$$

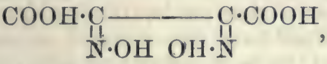
is obtained when the β-compound described above is hydrolysed with soda in the cold, the solution acidified and extracted with ether. It melts at 88° with decomposition, and is more sparingly soluble in water, alcohol, and ether than the α-acid; it is insoluble in benzene, chloroform, and light petroleum. It turns red on exposure to the air, either in the dry state or in aqueous solution, and it gives a characteristic blue coloration with ferric chloride; in neutral ammoniacal solutions, most metallic salts produce colourless precipitates, the silver salt being very explosive. When the acid is heated at about 40° in concentrated aqueous solution, carbonic anhydride is evolved, and, on evaporating, cyanoacetic acid remains as a colourless, deliquescent, crystalline mass; the same decomposition takes place to a considerable extent when the β-oximido-acid is kept for some time over potash at the ordinary temperature; its acid solutions are also unstable even at the ordinary temperature, but its alkaline solutions can be boiled without undergoing any change.

When the ethyl hydrogen salt of the α-acid is treated with concentrated sulphuric acid, acetic chloride, or acetic anhydride, it is converted into the corresponding β-compound; the α-dicarboxylic acid is also converted into the β-derivative on treatment with concentrated sulphuric acid.

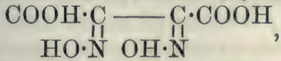
β-Oximidosuccinic anhydride,  $OH\cdot N{:}C<\begin{matrix}CO\cdot O\\ CH_2\cdot CO\end{matrix}$, is formed when the β-acid is treated with acetic chloride; it forms colourless crystals, softens at 95°, and melts completely at 105° with decomposition. It is only moderately easily soluble in water, being thereby converted into the acid, but when heated alone it is readily decomposed into carbonic anhydride and cyanoacetic acid. The *acetyl* derivative  $OAc\cdot N{:}C<\begin{matrix}CO\cdot C\\ CH_2\cdot CO\end{matrix}$, prepared by treating the anhydride, or the acid, with acetic anhydride, forms large, colourless crystals, melts at 105° with decomposition, and is readily decomposed by water.

When the α-acid is treated with acetic chloride or with acetic anhydride, it yields products identical with those obtained from the β-acid in like manner, and which, on decomposition with water, yield the β-acid. F. S. K.

Dioximidosuccinic Acids. By H. G. Söderbaum (*Ber.*, **24**, 1215—1235).—According to the theory of Hantzsch and Werner, there are three dioximidosuccinic acids capable of existence. The author has succeeded in preparing two of these compounds; the one is doubtless the αα-dioxime of the configuration  $\begin{matrix}COOH\cdot C\cdot C\cdot COOH\\ \| \quad \|\\ OH\cdot N\ N\cdot OH\end{matrix}$; the other is probably the ββ-dioxime of the configuration



$$\begin{matrix}COOH\cdot C \text{———} C\cdot COOH\\ \| \qquad\qquad \|\\ N\cdot OH\quad OH\cdot N\end{matrix},$$

whilst the third isomeride, namely, the αβ-dioxime of the configuration  $\begin{matrix}COOH\cdot C \text{——} C\cdot COOH\\ \| \qquad \|\\ HO\cdot N\quad OH\cdot N\end{matrix}$, could not be obtained. The various reactions which throw light on the constitution of the two dioximes are described below (compare Hantzsch, this vol., p. 439).

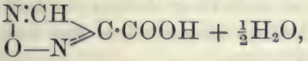
ββ-Dioximidosuccinic acid (dihydroxytartaric acid ββ-dioxime) has been previously prepared by Müller (Abstr., 1884, 584), who named it diisonitrososuccinic acid; although the method of preparation employed by Müller gives a very pure product, it occupies rather a long time, and the yield is only about 20 per cent. of the theoretical. The following method was found to be more convenient:—A mixture of commercial sodium dihydroxytartrate (1 mol.) and a slight excess of the theoretical quantity (2 mols.) of hydroxylamine hydrochloride is dissolved in the least possible quantity of cold, dilute hydrochloric acid of sp. gr. 1·03—1·04, the solution kept for about 12 hours at the ordinary temperature, filtered if necessary, and extracted 10 to 12 times with ether; the ethereal solution is dried over anhydrous sodium sulphate, about four-fifths of the ether evaporated on the water-bath, the residual solution cooled with ice and evaporated over sulphuric acid under reduced pressure. As soon as crystallisation commences, dry chloroform (about 3 parts) is added with constant stirring, when the dioxime is almost completely deposited in crystals, whilst the furazancarboxylic acid, which is also produced, remains in solution. The colourless, crystalline product is quickly separated by filtration, pressed, and recrystallised from a mixture of ether and chloroform, from which it separates in large, colourless, transparent prisms containing 2 mols. H_2O, and melting at about 90°; the yield is about 30 per cent. of the theoretical. It is deposited from aqueous solutions in crystals containing 4 mols. H_2O, which melt at 70—75°, and from ether it separates in crystals containing a quantity of water varying from 2 to 4 mols.; the crystals lose the whole of their water over sulphuric acid, the anhydrous compound melting at 145—150° with decomposition. $\beta\beta$-Dioximidosuccinic acid is very readily soluble in water, alcohol, and ether, but insoluble in benzene, chloroform, and light petroleum; it has acid properties, turns red litmus blue, and decomposes carbonates, but is also readily soluble in acids. The silver salt, $C_4H_2N_2O_6Ag_2$, crystallises in long, colourless needles melting at 140—150° with decomposition. The *calcium* salt, $C_4H_2N_2O_6Ca + 4H_2O$, is deposited in microscopic, hexagonal plates on adding calcium acetate to a moderately concentrated solution of the acid; it loses 2 mols. H_2O at 95—100°, and is gradually decomposed at a higher temperature. In aqueous solutions of the acid, barium acetate produces no precipitate, but barium hydroxide gives a colourless, ferric chloride a dark red, and copper acetate a dirty green precipitate which soon turns brown; on adding a little soda and then ferrous sulphate to a solution of the acid, an intense violet coloration is produced. The acid crystallises unchanged from boiling water, but it is unstable towards acids, being thereby converted into the $\alpha\alpha$-dioximido-compound. The *diacetyl* derivative, $C_4H_2N_2O_4(OAc)_2$, is obtained in colourless needles or rhombic plates, when the pure anhydrous acid is kept in contact with acetic anhydride at 0° until dissolution is complete, and the excess of anhydride then evaporated over potash; it melts at about 150° with decomposition, gradually decomposes on exposure to the air with liberation of acetic acid, and is readily soluble in water, alcohol, and ether, but is insoluble in benzene. The *silver* salt is precipitated in well-defined rectangular plates on adding silver nitrate to a freshly prepared aqueous solution of the diacetyl derivative. When an aqueous solution of the diacetyl derivative is evaporated at the ordinary temperature, it is completely decomposed and the $\beta\beta$-dioxime is deposited in crystals; the diacetyl derivative is also decomposed by soda or sodium carbonate into furazancarboxylic acid (see below) and carbonic anhydride.

When $\beta\beta$-dioximidosuccinic acid is treated with excess of acetic chloride at the ordinary temperature, it gradually passes into solution, and on evaporating the excess of acetic chloride over potash, there remains an almost colourless oil, from which, in some experiments, a small quantity of a crystalline compound was gradually deposited; this oil is doubtless an acetyl derivative, but it was not analysed; it is quickly decomposed by water, being thereby converted into the $\alpha\alpha$-dioxime, and when treated with sodium carbonate, or with dilute soda, it is transformed into furazancarboxylic acid.

αα-Dioximidosuccinic acid is most conveniently prepared by dissolving the ββ-compound in a little concentrated hydrochloric acid, and keeping the solution for some time at the ordinary temperature, when the αα-dioxime is gradually deposited in crystals; it is also formed when the ββ-compound is treated with hydrogen chloride, or with phosphorus pentachloride, in ethereal solution. It usually separates from a mixture of chloroform and ether as an oil, which then solidifies to a mass of crystals, having the composition $C_4H_4N_2O_6 + 2H_2O$; these crystals lose their water at 40—45°, the anhydrous substance melting at 145—150° with decomposition. It is very readily soluble in water, alcohol, and ether, but insoluble in chloroform, benzene, and light petroleum; as regards chemical behaviour and the solubility of its salts, it resembles closely the isomeride just described. The *silver* salt, $C_4H_2N_2O_6Ag_2 + H_2O$, prepared by adding silver nitrate to an aqueous solution of the acid, is a colourless, granular compound moderately stable in the light; it loses its water at 60°, melts at 145—150°, and explodes violently at about 153°. The *calcium* salt, $C_4H_2N_2O_6Ca + 3H_2O$, is precipitated in colourless, microscopic prisms on adding calcium acetate to a solution of the acid; it loses only part of its water at 100°. An aqueous solution of the αα-acid gives the same reactions with ferrous sulphate and with ferric chloride as the ββ-compound, but with copper acetate there is produced a green, amorphous precipitate.

αα-Dioximidosuccinic acid is not decomposed by boiling dilute alkalis, but when treated with acetic anhydride at the ordinary temperature, it is gradually and completely decomposed into water, cyanogen, and carbonic anhydride. On treatment with acetic chloride, it yields a colourless oil which, in all probability, is identical with the compound obtained in like manner from the ββ-derivative; this oil is reconverted into the αα-dioximido-acid by cold water, but alkalis decompose it into furazancarboxylic acid and carbonic anhydride.

Furazancarboxylic acid (*azoxazolecarboxylic acid*),



$$\begin{matrix}\mathrm{N{:}CH} \\ | \\ \mathrm{O{-}N}\end{matrix}\!\!>\!\mathrm{C{\cdot}COOH} + \tfrac{1}{2}H_2O,$$

is obtained in the preparation of ββ-dioximidosuccinic acid as described above, and is isolated by evaporating the ethereal chloroform mother liquors from the dioxime; the yellow oil obtained in this way gradually solidifies and can then be recrystallised from cold chloroform; it is best prepared in a pure condition by treating either of the dioximido-acids with acetic chloride, and decomposing the product with soda or sodium carbonate. It crystallises in colourless needles, melts at 101—102° with decomposition, and is very readily soluble in water, alcohol, and ether, and moderately easily in chloroform, but insoluble in benzene and light petroleum; it cannot be obtained in an anhydrous condition either by recrystallisation from dehydrating solvents or by careful heating. It dissolves in soda yielding a yellow solution, from which it is precipitated unchanged on acidifying, and it is not decomposed by cold concentrated sulphuric acid, but, on prolonged boiling with dilute hydrochloric acid, it is completely destroyed, the principal product being oxalic acid; it is completely decomposed when heated at 100°, a strong odour of cyanogen being observed, and when treated with potassium permanganate at the ordinary temperature, it is completely destroyed, carbonic anhydride, cyanogen, and nitric acid being formed. The *silver* salt, $C_3HN_2O_3Ag$, is precipitated in colourless, granular crystals, on adding silver nitrate to an aqueous solution of the acid, but from neutral aqueous solutions a yellow, crystalline, explosive salt of the composition $C_3N_2O_3Ag_2$ is precipitated; on adding copper acetate to a moderately concentrated solution of the acid, a dark-green solution is obtained, and after a short time a copper compound is deposited in well-defined plates, which explode violently when heated. The acid is not acted on by acetic anhydride at the ordinary temperature, but when heated therewith it is completely decomposed; attempts to prepare an acetyl derivative with the aid of acetic chloride were also unsuccessful.

F. S. K.

Trimethylsuccinic Acid. By C. A. BISCHOFF (*Ber.*, **24**, 1041—1049).—No definite compound could be obtained by the action of sodium ethoxide on ethyl α-bromisobutyrate. On treatment with alcoholic potash, however, α-ethoxyisobutyric acid, methylacrylic acid, and α-hydroxyisobutyric acid are formed. *Methyacrylic anilide*, $CH_2{:}CMe{\cdot}CO{\cdot}NHPh$, crystallises from dilute alcohol in lustrous prisms, and melts at 120°.

Ethyl α-bromisobutyrate, on treatment with concentrated aqueous ammonia at low temperatures yields a crystalline *amide* of the formula $CMe_2Br{\cdot}CONH_2$, which melts at 147°. By the action of aniline at 0°, an anilide is formed in small quantity, which crystallises in needles and remains unmelted at 250°; on heating the isobutyrate with aniline (2 mols.) at 150—160°, ethyl α-anilidisobutyrate, $NHPh{\cdot}CMe_2{\cdot}COOEt$, is obtained. *α-Bromisobutyric anilide*, $CMe_2Br{\cdot}CO{\cdot}NHPh$, is formed quantitatively by the action of aniline on α-bromisobutyric bromide in benzene solution at the ordinary temperature; it crystallises from dilute alcohol and melts at 83°; a proof is thus afforded of the freedom of the ethyl α-bromisobutyrate from any β-bromo-derivative.

Trimethylsuccinic acid is prepared by treating ethyl sodiomethylmalonate with ethyl α-bromisobutyrate for 5 hours at 180—190° under pressure, the product is washed with water, distilled, and the portion boiling at 275—285° hydrolysed with alcoholic potash, the acid thus obtained is heated at 200° until carbonic anhydride ceases to be evolved, the residue is distilled, and the portion passing over up to 250° recrystallised, first from chloroform, then from benzene and light petroleum; the acid melts at 139·5°, its electrolytic conductivity is $M_\infty = 351$; $k = 0{\cdot}031$, and it is in all respects identical with the trimethylsuccinic acid of Zelinsky and Besredka (this vol., p. 669). The higher fractions (b. p. 260—280°), separated during the distillation after hydrolysis, consist of symmetrical dimethylglutaric acid (m. p. 102—105°).

The acid (m. p. 106°) previously prepared by the author and Hell from amylene bromide, and termed trimethylsuccinic acid, is in all probability asymmetrical ethylmethylsuccinic acid,

$COOH{\cdot}CH_2{\cdot}CEtMe{\cdot}COOH$. J. B. T.

Substituted Dimethylsuccinic Acids. By C. A. Bischoff (*Ber.*, **24**, 1050—1064).—It has previously been shown (this vol., p. 290) that ethyldimethylsuccinic acid, $COOH{\cdot}CHEt{\cdot}CMe_2{\cdot}COOH$, may be prepared by the action of ethyl α-bromisobutyrate on ethyl sodioethylmalonate; considerable quantities of ethylmethylglutaric acid, $COOH{\cdot}CHEt{\cdot}CH_2{\cdot}CHMe{\cdot}COOH$, are also formed during the reaction. The succinic acid gives a white precipitate with potassium aluminium sulphate, and with lead, mercury, and zinc salts; copper sulphate produces a green, flocculent precipitate, and ferric chloride a yellowish-brown one. The electrolytic conductivity has been redetermined, and found to be $M\infty = 351$; $k = 0{\cdot}056$. All attempts to convert the acid into an isomeric form were fruitless.

Ethylmethylcarboxyglutaric acid, $COOH{\cdot}CHMe{\cdot}CH_2{\cdot}CEt(COOH)_2$, melts at 166·5° with evolution of carbonic anhydride, and is almost insoluble in light petroleum or carbon bisulphide; the *silver*, *mercury*, and *lead* salts are white and insoluble.

Parethylmethylglutaric acid crystallises from water in aggregates of small, slender needles, melts at 105°, and is insoluble in carbon bisulphide or xylene. The *lead*, *silver*, *aluminium*, *cupric*, *ferric*, and *zinc* salts are sparingly soluble; the last is crystalline, and is only precipitated on warming.

The meso-acid closely resembles the para-acid, from which it is separated by fractional crystallisation from water; it is deposited in concentric needles melting at 61°.

A mixture of these acids may be prepared by the following method, which also serves to show that they are actually glutaric acids. Ethyl sodiodicarboxygluconate,

$$CNa(COOEt)_2{\cdot}CH{:}C(COOEt)_2,$$

is treated with ethyl iodide, and the product reduced; the sodium derivative of the resulting ethyl ethyldicarboxyglutarate is treated with methyl iodide, and the ethyl methylethyldicarboxyglutarate, $CEt(COOEt)_2{\cdot}CH_2{\cdot}CMe(COOEt)_2$, thus obtained is hydrolysed; the acid melts at 150—170° with evolution of carbonic anhydride, and, after the complete elimination of this, crystals are deposited which melt at 70—76°, and behave in every way like a mixture of para- and meso-ethylmethylglutaric acid.

Propyldimethylsuccinic acid, $COOH{\cdot}CMe_2{\cdot}CHPr^{\alpha}{\cdot}COOH$, is prepared from ethyl sodiopropylmalonate and ethyl α-bromisobutyrate, and crystallises from water in slender, rhombic needles; it is insoluble in light petroleum or carbon bisulphide, and melts at 140°. The electrolytic conductivity is $M\infty = 350$; $k = 0{\cdot}055$. It was not found possible to convert the acid into an isomeric modification. The *calcium*, *cadmium*, *zinc*, *aluminium*, *ferric*, *cupric*, *mercuric*, *lead*, and *silver* salts are all more or less insoluble.

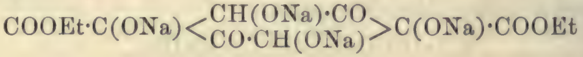
Benzyldimethylsuccinic acid, $COOH{\cdot}CH(C_7H_7){\cdot}CMe_2{\cdot}COOH$, is obtained from ethyl sodiobenzylmalonate and ethyl α-bromisobutyrate by heating for 10 hours at 190—205° under a pressure of 5—6 atmos.;

the acid crystallises from water in short, prismatic needles and melts at 140°; on heating at 152°, water is eliminated. The electrolytic conductivity is $M_\infty = 350$; $k = 0{\cdot}046$. Like the preceding acids, this could not be converted into an isomeride. The *calcium* salt is deposited in needles; the *zinc*, *mercuric*, *lead*, and *silver* salts are crystalline; the *aluminium* and *ferric* salts flocculent.

On heating benzyl chloride with ethyl sodioisobutylenetricarboxylate in xylene solution for 12 hours under a pressure of 5—6 atmos., dibenzylmalonic acid is formed in considerable quantity; the highest boiling portion of the product consists of ethyl benzylisobutenyltricarboxylate, whilst the lowest fraction probably contains methylacrylic acid; no benzyldimethylsuccinic acid or benzylmethylglutaric acid could be detected. J. B. T.

Transformation of Ethyl Disodiotartrate by Ethyl Chloride. By E. MULDER (*Rec. Trav. Chim.* [9], **5**, 238—275).—After some time, a solution of ethyl disodiotartrate in ethyl chloride yields a precipitate. The decanted mother liquor, freed from excess of ethyl chloride, and evaporated to dryness in an atmosphere of hydrogen under reduced pressure, gives a yellow, amorphous residue. This substance, dissolved in absolute ether, is recovered unaltered on evaporation of the solvent. It contains ethyl chloride, which is given off in a vacuum, leaving a product which gelatinises in damp air, and, in aqueous or alcoholic solutions, is coloured cherry-red by ferric chloride. On heating in an atmosphere of hydrogen under reduced pressure at about 90°, no ethyl chloride comes off, but about 10 per cent. of a gas, probably ethylene, is evolved.

The main constituent of the yellow, amorphous mass appears to have the composition



$$COOEt\cdot C(ONa)<\begin{matrix}CH(ONa)\cdot CO\\ CO\cdot CH(ONa)\end{matrix}>C(ONa)\cdot COOEt$$

+ 1½ molecular proportions of ethyl chloride, which are not lost when the compound is kept under diminished pressure. The yellow colour is probably due to the presence of a coloured impurity. The ethereal solution of this substance, when treated with hydrogen chloride, yields ethyl pyruvate.

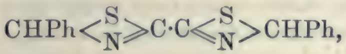
The author concludes, from the results of his experiments, that a system of equilibrium exists between ethyl disodiotartrate, ethyl chloride, alcohol, and the substance formed in the reaction. Alcohol retards, ethyl chloride accelerates, the transformation.

It is claimed that by the use of ethyl chloride as a solvent for such substances as ethyl disodiotartrate, the study of many reactions is rendered possible. W. T.

Acetyliodobenzene and Iodomandelic Acid. By R. SCHWEITZER (*Ber.*, **24**, 997; compare this vol., p. 729).—The acetyliodobenzene recently described (this vol., p. 684) is probably identical with pariodacetophenone (m. p. 79°); when treated with bromine in carbon bisulphide solution, it is converted into the dibromo-derivative, $C_6H_4I\cdot CO\cdot CHBr_2$, which melts at 86°.

Iodomandelic acid, $C_6H_4I{\cdot}CH(OH){\cdot}COOH$, is obtained when this bromo-derivative is treated with potash (1 : 10) at the ordinary temperature. It melts at 135°, and is readily soluble in water, alcohol, and ether, but only sparingly in light petroleum; the barium salt is readily soluble. F. S. K.

Action of Aldehydes on Thioamides. By J. EPHRAIM (*Ber.*, **24**, 1026—1031).—*Dibenzylidenedithioxamide*,



$$\mathrm{CHPh}<\begin{matrix}\mathrm{S}\\ \mathrm{N}\end{matrix}\geqslant\mathrm{C{\cdot}C}\leqslant\begin{matrix}\mathrm{S}\\ \mathrm{N}\end{matrix}>\mathrm{CHPh},$$

is formed when dithioxamide (1 gram) is heated to boiling with benzaldehyde (9 grams) in a reflux apparatus. The crystalline mass so obtained is dried on a porous plate, and crystallised from benzene or acetic acid. It crystallises in yellowish-white needles, melts at 209°, is a very indifferent substance, and does not dissolve in aqueous soda or hydrochloric acid. The sulphur is not displaced when the compound is treated with mercury oxide. It is not resolved into its components when heated with hydrochloric acid in a sealed tube; methyl iodide has no action on it. When oxidised with permanganate or chromic acid, benzoic acid, ammonia, and sulphuric acid are formed.

Dioxydibenzylidenedithioxamide, $C_{16}H_{12}S_2N_2O_2$, is obtained from salicylaldehyde and dithioxamide in a similar way to the above. It dissolves in caustic soda to an orange-yellow solution, is reprecipitated by acids, and crystallises from chloroform. The *benzoyl compound*, $C_{16}H_{10}S_2N_2O_2Bz_2$, is pale-yellow, and melts at 156°.

Dinitrodibenzylidenedithioxamide, $C_{16}H_{10}S_2N_4O_4$, is obtained by warming dibenzylidenedithioxamide with nitric acid (sp. gr. = 1·50). It is a lemon-yellow compound, crystallises from boiling aniline, and melts at 269°. On oxidation with chromic acid, it yields paranitrobenzoic acid, ammonia, and sulphuric acid. It is not reduced by tin and hydrochloric acid, nor by zinc and acetic acid. When heated with hydriodic acid (1·7) and phosphorus for some hours at 190° in a sealed tube, it yields hydrogen sulphide and amidobenzylamine.

Dibenzylidenedithioxamide, when reduced with hydriodic acid, did not yield benzylamine, but benzoic acid. The author supposes that benzonitrile is first formed, and that this is then hydrolysed by the hydriodic acid to benzoic acid. He is at present engaged in further examination of this reaction.

The stability of these compounds towards acids shows that they are not analogous to the compounds formed from acid amides and aldehydes, which latter are easily decomposed into their components. The behaviour of the nitro-compound on reduction with hydriodic acid and phosphorus shows that the nitrogen of the dithioxamide is combined with the benzaldehyde residue. Hence, the author concludes that the above formula of dibenzylidenedithioxamide is correct. And he points out that dithioxamide behaves in this reaction as if its constitution were $NH{:}C(SH){\cdot}C(SH){:}NH$.

Thiobenzamide reacts with benzaldehyde and salicylaldehyde to form compounds which do not contain sulphur. Thioacetanilide does not react with benzaldehyde. E. C. R.

Theory of Dyeing. By L. VIGNON (*Compt. rend.*, **112**, 623—624).—The author has previously shown (Abstr., 1890, 553, 939) that animal fibres, which dye easily, have well marked acidic or basic functions, whilst in vegetable fibres, which dye with difficulty, such functions are very feeble; that cotton, when heated with ammonia takes up nitrogen, acquires a basic function, and dyes readily with acid colouring matters (this vol., p. 662); that the power of stannic acid to combine with basic colouring matters is proportional to the energy of the acidic function of the acid (this vol., p. 807). Moreover, all the mordants employed in dyeing are either basic or acidic oxides. All soluble colouring matters natural and artificial, contain a salifiable group, OH, or a basic group, NH_2, or acidic group, NO_2. No true colouring matter is known which consists of a hydrocarbon only or which has not a basic or an acidic function, or both, with or without the functions of an alcohol, ketone, or aldehyde.

The author concludes that dyeing with soluble colouring matters and textile fibres or metallic oxides is a process of a purely chemical order, and depends essentially on the presence of basic and acidic functions in the colouring matter and its absorbent.

The only exception to this law is the group of tetrazoic colours which dye cotton in an alkaline bath without a mordant, but this group requires special investigation. C. H. B.

Allocinnamic Acid. By C. LIEBERMANN (*Ber.*, **24**, 1101—1110).—The author has not, as yet, carried out his purpose of fully examining the relationships of isocinnamic acid and allocinnamic acids, owing to his inability to obtain a fresh supply of the former compound. This may be due to the fact that the raw material employed did not contain any isocinnamic acid, or to the fact that it is converted into allocinnamic acid in the modified process employed for its purification. In place of the method previously described (Abstr., 1890, 1417), about 1 kilo. of the raw material was dissolved in 10 litres of water, boiled with a slight excess of milk of lime for 24 hours, allowed to cool, and filtered; the filtrate, after concentration to 2½ litres, was again separated from the precipitated calcium salts, acidified with hydrochloric acid, and extracted with ether. After evaporating off the latter, the residue was treated with light petroleum, and the product remaining on its evaporation, dissolved in benzene and treated with aniline. Aniline allocinnamate separates out as a magma of voluminous needles, which are filtered off, washed with light petroleum, and acidified with hydrochloric acid; the allocinnamic acid is extracted with ether, and after evaporating off the latter, recrystallised from light petroleum.

The crystals of allocinnamic acid obtained had the melting point previously found, namely 68°, and on crystallographic examination were found to have the same measurements as the original specimen, although the development differed considerably. Aniline allocinnamate $(C_9H_8O_2)_2,C_6H_7N$, has the same melting point and composition as the compound obtained from aniline and isocinnamic acid, and it appears extremely probable that isocinnamic acid is converted by the action of aniline and subsequent treatment with acid into allocinnamic acid. If this is the case, the fact that no isocinnamic acid was obtained with the new method of purification is readily understood, and, according to a private communication to the author, Erlenmeyer has also found that the isocinnamic acid obtained from β-bromocinnamic acid is, in fact, converted into allocinnamic acid by this treatment. It would, therefore, appear probable that isocinnamic acid is a dimorphous, very labile form of allocinnamic acid; in confirmation of this, is the fact that the crystals of isocinnamic acid previously measured had undergone a change, and, on washing with light petroleum and then recrystallising from this liquid, had the melting point of allocinnamic acid.

Paratoluidine allocinnamate, $(C_9H_8O_2)_2.C_7H_9N$, is obtained by the direct union of the acid and base in benzene solution; it crystallises from water in silky, colourless needles and melts at 79—80°. *Phenylhydrazine allocinnamate*, $C_9H_8O_2,C_6H_8N_2$, forms colourless needles or plates and melts at 74°, whilst *tropine allocinnamate*, $C_9H_8O_2.C_8H_{15}NO$, separates first as an oil, and then solidifies to beautiful crystals, having a neutral reaction and melting at 138°.

The following compounds were also prepared for the sake of comparison:—*Phenylhydrazine cinnamate*, $C_9H_8O_2,C_6H_8N_2$, melting at 110°, and much less soluble in water and benzene than the allocinnamate; *phenylhydrazine hydrocinnamate*, crystallising in silky needles and melting at 57°; and *tropine cinnamate*, which is an oil.

Methyl allocinnamate, $C_9H_7O_2Me$, is obtained by acting on the silver salt with methyl iodide, and forms a colourless, strongly refractive oil, the odour of which is similar to that of methyl isocinnamate and melted methyl cinnamate. By very careful addition of bromine in carbon bisulphide solution, it yields a mixture of the dibromide of methyl cinnamate with a little of the dibromide of methyl isocinnamate. The former crystallises out first, and the mother-liquor is then evaporated and treated with light petroleum, which dissolves out the allo-compound; this crystallises in cauliflower-shaped nodules melting at 52—53°. Both dibromides lose the added bromine on treatment with zinc turnings and alcohol, the first yielding methyl cinnamate, and the second a mixture of methyl cinnamate and methyl allocinnamate in the proportion of ten of the former to one of the latter. By more careful working, the quantity of the latter might probably be increased. H. G. C.

Amidotolyloxamic Acid. By H. SCHIFF and A. VANNI (*Ber.*, **24**, 870—873).—The authors have already shown that in metatoluylenediamine the amido-group in the para-position to the methyl group is first attacked by acid residues (this vol., p. 702).

Amidotolyloxamic acid, $NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}C_2O_2{\cdot}OH$ [1 : 2 : 4], is obtained, together with ethyl amidotolyloxamate, by boiling a solution of toluylenediamine and ethyl oxalate in 90—94 per cent. alcohol for some days in a reflux apparatus. The two compounds are separated by means of alcohol, in which the acid is only slightly soluble. It can also be obtained by boiling an alcoholic solution of the diamine with dehydrated oxalic acid. The acid is colourless, is insoluble in water, sparingly soluble in boiling alcohol, easily soluble in dilute acids and alkalis, and melts at 223° with decomposition. The *potassium* salt forms easily soluble, colourless scales.

Amidotolyloxamide, $NH_2\cdot C_6H_3Me\cdot NH\cdot C_2O_2\cdot NH_2$ [1 : 2 : 4], is obtained by adding alcoholic ammonia to an alcoholic solution of ethyl amidotolyloxamate. It crystallises from alcohol in shining scales, melts at 223°, dissolves easily in hydrochloric acid, and yields a crystalline platinochloride. Amidotolyloxamide is also formed when toluylenediamine and ethyl oxamate are heated together at 110–115°, and by boiling a dilute alcoholic solution of toluylenediamine with ethyl oxamate. In concentrated solution, however, a large quantity of ethyl amidotolyloxamate is formed.

Amidotolyloxanilide, $NH_2\cdot C_6H_3Me\cdot NH\cdot C_2O_2\cdot NHPh$ [1 : 2 : 4], is obtained by boiling ethyl amidotolyloxamate or amidotolyloxamide with aniline, or by melting toluylenediamine with ethyl phenyloxamate. It crystallises from alcohol and dilute acetic acid, and melts at 185—186°. It is only a feeble base and the hydrochloride easily loses half its acid.

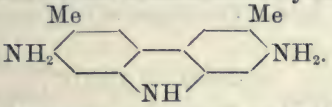
The amido-group of amidotolyloxamic acid is not attacked by ethyl oxalate unless the alcoholic solution of the two substances is heated in a sealed tube at 120°. The ethereal salts of the acid are, however, easily acted on by ethyl oxalate, and the dioxal compound, $C_7H_6(NH\cdot C_2O_2\cdot OEt)_2$, is obtained.

Urethanotolyloxamic acid, $COOEt\cdot NH\cdot C_6H_3Me\cdot NH\cdot C_2O_2\cdot OH + \frac{1}{2}H_2O$, is obtained by the action of ethyl chlorocarbonate on finely powdered potassium amidotolyloxamate under ether. The reaction must be completed by heating in a reflux apparatus. The acid forms small, colourless plates, melts at 168—170°, and dissolves easily in alcohol, not so easily in water. The aqueous solution tastes slightly sweet. By the action of ammonia, the urethane group is not converted into the uramido-group.

Uramidotolyloxamic acid, $NH_2\cdot CO\cdot NH\cdot C_6H_3Me\cdot NH\cdot C_2O_2\cdot OH$, is obtained by the action of potassium cyanate on finely powdered amidotolyloxamic acid suspended in water and precipitation with hydrochloric acid. It is a white, crystalline powder, slightly soluble in water, and melts at 203°. The *ethyl* salt is obtained in a similar way from ethyl amidotolyloxamate. E. C. R.

Synthesis of Carbazole Derivatives. By E. Täuber and R. Loewenherz (*Ber.*, **24**, 1033—1036).—One of the authors has described the synthesis of diamidocarbazole and carbazole from benzidine (this vol., pp. 227 and 570). The present paper deals with the synthesis of homologues of carbazole from orthotolidine.

Diamidodimethylcarbazole.—Orthotolidine is easily converted into metadinitro-orthotolidine as described by Gerber; and the latter compound, on reduction with tin and hydrochloric acid, yields metadiamidorthotolidine. The hydrochloride of this base is precipitated from concentrated aqueous solution by strong hydrochloric acid as a white, crystalline powder. To obtain diamidodimethylcarbazole, the hydrochloride is heated with 20 per cent. hydrochloric acid (3—4 parts) in a sealed tube at 190—200° for 15 hours. The product is purified by treating the aqueous solution with tin chloride and hydrogen sulphide, concentrating the filtrate by rapid boiling in a flask, and precipitating with hydrochloric acid; on cooling, the diamidodimethylcarbazole hydrochloride crystallises in pure white needles. The yield is 75 per cent. of that required by theory. The *sulphate* is obtained by adding sulphuric acid to a somewhat concentrated solution of the hydrochloride, and also in colourless needles (0·5 cm. long) on adding sodium sulphate to a dilute neutral solution. The base is obtained in white, microscopic needles by precipitating a hot, very dilute, solution of the hydrochloride. It is insoluble in water, sparingly soluble in cold alcohol, benzene, toluene, and ether, and more soluble in the hot solvents, crystallises from alcohol in small, colourless needles, blackens at 260°, and melts at 271°. Both the base and its salts, when moist, become coloured on exposure to air. The *diacetyl* compound, obtained by boiling the base with acetic acid (5 parts) for 6 hours, crystallises from acetic acid in slender, colourless needles, and melts above 300°. In accordance with the above synthesis, the constitution of the diamidodimethylcarbazole is represented by the formula



Dimethylcarbazole is obtained by heating orthodiamidoditolyl with 20 per cent. hydrochloric acid at 200°; and also from the above diamidodimethylcarbazole by eliminating the amido-groups. It closely resembles carbazole in appearance, solubility, crystalline form, and capacity for volatilisation. The picrate crystallises in reddish-brown needles and melts at 192°. The dimethylcarbazole regenerated from the latter, after crystallisation from benzene and sublimation, melts at 219°. Whilst a solution of carbazole in sulphuric acid is coloured greenish-blue by nitrous acid in the cold, a sulphuric acid solution of dimethylcarbazole is coloured pale brownish-yellow, and after a time or on warming, a pure blue. Chromic acid colours the sulphuric acid solution of carbazole deep blue: but a solution of dimethylcarbazole is coloured brown. On heating dimethylcarbazole with oxalic acid, no characteristic dye is obtained; carbazole on similar treatment yields a blue dye. The authors point out that these results tend to confirm the conclusion of Bamberger and Müller that carbazole-blue is a derivative of triphenylmethane, since in dimethylcarbazole the para-positions to the imido-group are occupied.

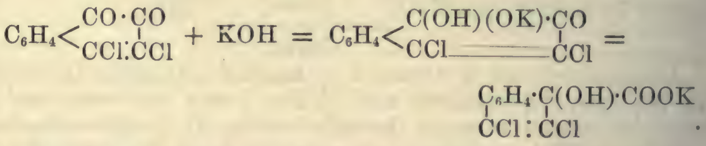
E. C. R.

Transformation of α-Diketones in Alkaline Solution. By S. Hoogewerff and W. A. van Dorp (*Rec. Trav. Chim.*, **9**, 225—237). —The reaction indicated by the equations $COPh{\cdot}COPh + KOH = OH{\cdot}CPh_2{\cdot}COOK$ is explained by the authors as brought about by an intramolecular transposition; thus the first stage consists of the production of $OH{\cdot}CPh(OK){\cdot}COPh$; the groups Ph and OK attached to contiguous carbon atoms are then interchanged with the production of $OH{\cdot}CPh_2{\cdot}COOK$. Numerous other examples of this transformation of α-diketones under the influence of hot potash are quoted.

Similar reactions have been explained in this way previously. Kekulé (*Annalen*, **221**, 238) accounts for the formation of sodium tartronate on heating the sodium salt of dihydroxytartaric acid by the intermediate formation of dihydroxypyruvic acid, and the transformation of the latter into tartronic acid by the exchange of H and (OH) between contiguous carbon atoms.

This transformation occurs also in the change of glyoxal into glycollic acid (Debus, *Annalen*, **102**, 26), and of benzoylformic acid into phenylglycollic acid (Engler and Wöhrle, Abstr., 1887, 948). The formation of lactic acid by the action of water on dichloracetone (Linnemann and v. Zotta, *Annalen*, **159**, 247) seems also to belong to the same class of reactions. This reaction is not general for diketones, failing in the case of diacetyl, although even in this case a similar reaction takes place when the symmetrical tetrachlorodiacetyl is heated with ammonia.

Zincke has found similar processes to take place with naphthalene derivatives containing the group (CO·CO) in the $\alpha\beta$-position; thus dichloro-β-naphthaquinone gives in alkaline solution dichlorindenehydroxycarboxylic acid. The stages of this reaction may be written—



$$C_6H_4{<}\begin{matrix}CO\cdot CO\\ CCl{:}CCl\end{matrix} + KOH = C_6H_4{<}\begin{matrix}C(OH)(OK)\cdot CO\\ CCl\text{———}CCl\end{matrix} = \begin{matrix}C_6H_4\cdot C(OH)\cdot COOK\\ CCl:CCl\end{matrix}.$$

Zincke has given a different explanation of the course of the reaction: by the assumption of 1 mol. of water and 1 mol. of potassium hydroxide the parent substance becomes

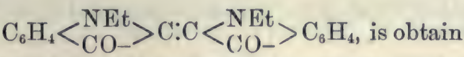
$$COOK\cdot C(OH)_2\cdot C_6H_4\cdot CCl{:}CHCl,$$

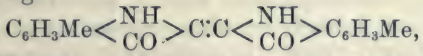
and this loses a molecule of water, yielding the final product as above. This method of viewing the mechanism of the change would require that in the formation of benzilic acid from benzile the diketone should split into C_6H_6 and $C_6H_5\cdot C(OH)_2\cdot COOH$, which afterwards unite to form the acid. The formation of croconic acid from rhodizonic acid, as also of tribromhydroxydiketopentamethylene from tetrabromotetraketohexamethylene, and some of Zincke and Küster's and of Hantzsch's results, admit of representation by the author's method.

The transformation of the α-glycols under the action of dehydrating agents, for instance of pinacone into $CMe_3\cdot CMe(OH)_2$, and the formation of pinacoline by the elimination of H_2O from this substance, comes under the same category. Volhard has given a similar explanation of the formation of benzyl alcohol and benzoic acid from benzaldehyde (*Annalen*, **253**, 238), but here we are dealing with an intermolecular reaction. The conclusion is drawn that forces of attraction exist between atoms in the molecule which are not represented in our formulæ as united; the resultant of these forces may bring about molecular transformations in many reactions which have not been otherwise explained. W. T.

Diethylindigo and Orthotolylindigo. By K. HEUMANN (*Ber.*, **24**, 977—979; compare this vol., pp. 206, 311, and 456).—Many of the derivatives of amidoacetic acid containing aromatic radicles are converted into leuco-compounds when heated with alkalis or alkaline earths; these leuco-compounds yield homologues or analogues of indigo on oxidation.

Ethylphenylamidoacetic acid, $\mathrm{NEtPh{\cdot}CH_2{\cdot}COOH}$, prepared by treating ethylaniline with chloracetic acid, is a thick, yellow oil, sparingly soluble in water.

Diethylindigo,  $\mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{NEt}{CO-}{>}C{:}C{<}\genfrac{}{}{0pt}{}{NEt}{CO-}{>}C_6H_4}$, is obtained when the preceding compound is heated with potash to about 360°, the mixture kept at this temperature for a few minutes, the brownish-red melt dissolved in water, and a stream of air passed through the solution. It is a dark-blue powder, and is probably identical with the compound obtained by Baeyer by reducing the diethyl derivative of pseudoisatin-α-oxime; it is sparingly soluble in hot alcohol, and dissolves in aniline yielding a bluish-green solution. The colours obtained on dyeing with diethylindigo and with its sulphonic acid are of a greener hue than those produced by indigo and indigo-carmine respectively. When the mixture of ethylphenylamidoacetic acid and potash is heated at 280—330° for 15 to 20 minutes, there is obtained a compound which, on oxidation, is converted into a substance having all the properties of indigo.

Orthotolylindigo,  $\mathrm{C_6H_3Me{<}\genfrac{}{}{0pt}{}{NH}{CO}{>}C{:}C{<}\genfrac{}{}{0pt}{}{NH}{CO}{>}C_6H_3Me}$, is formed when orthotolylamidoacetic acid is heated with potash (2 parts) at 300—350°, the melt dissolved in water, and a stream of air passed through the solution. It is only very sparingly soluble in boiling alcohol, yielding a deep-blue solution; it crystallises from hot aniline in slender, copper-red prisms. Cotton dyed with orthotolylindigo is of a slightly greener shade than that obtained with indigo. The sulphonic acid of orthotolylindigo is soluble in water, but is precipitated from the solution on adding sodium chloride; it dyes wool in an acid-bath, the shade obtained being of a redder hue than is the case with indigo-carmine. F. S. K.

Phenanthridine. By A. PICTET and H. J. ANKERSMIT (*Chem. Centr.*, 1891, i, 361—362; from *Arch. sci. phys. nat. Genève*, **24**, 598—606).—In addition to the synthesis of phenanthridine from benzylideneaniline (Abstr., 1890, 390), the authors have prepared it from orthophenylbenzoic acid. By nitrating this and reducing the resulting mixture of nitrophenylbenzoic acids with zinc powder and ammonia, the corresponding amido-acids are produced, from one only of which, namely, $\mathrm{NH_2{\cdot}C_{12}H_8{\cdot}COOH}$ [2 : 2′], can the new base be derived. The reduced mixture is extracted with boiling alcohol, which solution deposits hydroxyphenanthridine in needles, from which phenanthridine is obtained by distilling with zinc powder.

Phenanthridine methylhydroxide, $\mathrm{C_{13}H_9N,MeOH}$, is prepared from the methiodide, by adding a few drops of sodium hydroxide solution, and pouring the mixture into water, when the hydroxide separates in long needles melting at 109°; it dissolves in alcohol and ether with beautiful fluorescence.

Phenanthridine on reduction is converted into *dihydrophenanthridine*, $C_{13}H_{11}N$, which forms white needles melting at 90°, nearly insoluble in water, soluble in alcohol and ether with blue fluorescence. It reacts as a secondary base. The *nitroso*-derivative, $C_{13}H_{10}N{\cdot}NO$, is a pale-yellow oil, which gives Liebermann's reaction for nitrosamines. The *methyl* derivative, $C_{13}H_{10}NMe$, forms white needles, melts at 108°, and is soluble in alcohol and ether with violet fluorescence. The *acetyl* derivative, $C_{13}H_{10}NAc$, forms prisms, and melts at 108°.

J. W. L.

Pyridine Compounds. By R. Varet (*Compt. rend.*, **112**, 622—623).—When pyridine heated at 40° is saturated with zinc bromide, energetic action takes place, with considerable development of heat, and when the liquid cools, it deposits slender, prismatic needles of the compound $ZnBr_2,2C_5NH_5$. It is stable at 110°, and is very soluble in water and in pyridine.

Finely powdered anhydrous nickel bromide, when boiled with pyridine for an hour, is converted into a green powder of the composition $NiBr_2,4C_5NH_5$. This compound alters when exposed to air, loses pyridine when heated, and is very soluble in pyridine.

Cupric bromide acts energetically under similar conditions, and is converted into small, hard, deep-green crystals of the compound $CuBr_2,4C_5NH_5$. It alters very readily, and evolves a strong odour of pyridine. When heated, or when exposed to air, it loses pyridine, and becomes bright-green. It dissolves in water and in pyridine.

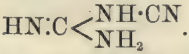
Silver iodide is dissolved by boiling pyridine, and the solution, when cooled, deposits lamellæ or prismatic needles of the compound AgI,C_5NH_5. It is somewhat soluble in pyridine, especially on heating, but is immediately decomposed by warm water, and more slowly by cold water; it alters when exposed to air, and loses all its pyridine when heated at 110°.

Silver bromide forms a similar compound, which crystallises in large, white, prismatic needles with a nacreous lustre. It is very unstable, and loses all its pyridine at 110°; it is soluble in cold pyridine, but is insoluble in water, and is decomposed by it.

Silver chloride is dissolved by cold pyridine, but on the addition of ether the unaltered chloride is precipitated, and there is no compound of silver chloride and pyridine stable at the ordinary temperature. The attraction of the silver halides for pyridine decreases as the molecular weight of the halogen increases.

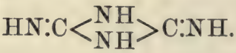
C. H. B.

Dicyanodiamide. By E. Bamberger and L. Seeberger (*Ber.*, **24**, 899—907).—Three formulæ have been proposed for dicyanodiamide, all of which equally well explain its behaviour. They are:—



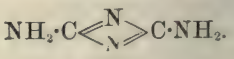
$HN{:}C{<}\begin{matrix}NH{\cdot}CN\\NH_2\end{matrix}.$

I.



$HN{:}C{<}\begin{matrix}NH\\NH\end{matrix}{>}C{:}NH.$

II.



$NH_2{\cdot}C{\ll}\begin{matrix}N\\N\end{matrix}{\gg}C{\cdot}NH_2.$

III.

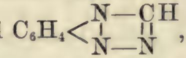
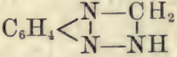
The author decides in favour of formula I, from a consideration of the behaviour of dicyanodiamide towards ammonia bases of the types N*abc* and *b*:N·*a*, when derivatives of biguanidine are formed.

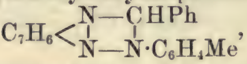
Copper piperylbiguanidine, $Cu[NH{\cdot}C(NH){\cdot}NH{\cdot}C(NH){\cdot}C_5NH_{10}]_2$, is obtained by heating dicyanodiamide (1·7 grams) and copper sulphate (2·5 grams) with piperidine (2 grams) and water (10 c.c.) for some hours at 100—120°. The reaction also takes place at the ordinary temperature, and is then complete in a few days. It is sparingly soluble in cold water, more so in hot water, and comes down as a fine, rose-red, crystalline powder, is insoluble in benzene, light petroleum, and ether, and easily soluble in ethyl alcohol, acetone, and amyl alcohol. The yield amounts to 65 per cent. of that required by theory.

Copper piperylbiguanidine sulphate, $(C_7H_{14}N_5)_2Cu,H_2SO_4$, is obtained by mixing the base with sulphuric acid in molecular proportion and warming the mixture on the water-bath. It crystallises from water in bright-red, shining needles, and blackens at 160° without melting. It is decomposed, by boiling with water, into copper oxide and piperylbiguanidine sulphate, $(C_7H_{15}N_5)_2,H_2SO_4$.

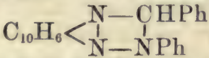
Piperylbiguanidine, $NH_2{\cdot}C(NH){\cdot}NH{\cdot}C(NH){\cdot}C_5NH_{10}$, is obtained by treating the above copper base, dissolved in dilute sulphuric acid, with hydrogen sulphide. On adding excess of aqueous soda to the filtrate, the piperylbiguanidine crystallises in silky needles, and melts at 163°. It is, however, rapidly converted into carbonate, and the melting point rises. It reacts strongly alkaline, absorbs carbonic anhydride from the air with avidity, is easily soluble in water and chloroform, sparingly in aqueous soda, ether, and benzene, and crystallises from hot alcohol in lustrous prisms. The *hydrochloride*, $C_7H_{15}N_5,2HCl$, crystallises from alcoholic solution in thick crusts, dissolves easily in water and alcohol, and, on the addition of ether to the latter solution, crystallises in slender needles, melts at 217°, and has an acid reaction. The *acid sulphate*, $C_7H_{15}N_5,H_2SO_4$, is obtained as a voluminous precipitate on adding sulphuric acid to an alcoholic solution of the base. It is obtained as a white, crystalline powder by precipitating a concentrated aqueous solution with alcohol, melts at 173°, and has an acid reaction, dissolves easily in water, sparingly in alcohol, and becomes electrical when rubbed. The *normal sulphate*, $(C_7H_{15}N_5)_2,H_2SO_4$, obtained from the mother liquors of the above salt, crystallises in beautiful, thick, colourless prisms, has a neutral, reaction, melts at 219°, and is easily soluble in water and alcohol. The *platinochloride*, $(C_7H_{15}N_5),H_2PtCl_6$, crystallises in lustrous, orange-red, rhombohedral prisms, is easily soluble in water, and melts at 252° with evolution of gas. The *aurochloride*, $C_7H_{15}N_5,2HCl,AuCl_3$, is obtained as a golden-yellow, lustrous precipitate consisting of slender needles.

E. C. R.

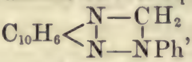
Derivatives of Orthamidoazo-compounds. By H. GOLDSCHMIDT and A. POLTZER (*Ber.*, **24**, 1000—1010).—The author has already described the compounds obtained by the combination of orthamidoazotoluene and benzeneazo-β-naphthylamine with benzaldehyde. These compounds differ essentially from the benzylidene derivatives of primary amines. They are not decomposed by hydrochloric acid at 150°, have distinctly basic properties, and are colourless. From their behaviour, the author concludes that they are compounds of the triazine series. Bischler (*Ber.*, **22**, 2806) has described the compound  $C_6H_4<\begin{array}{l}N-CH\\ |\quad\ \ \|\\ N-N\end{array}$, and named it phenotriazine. The compounds described by the authors are derivatives of dihydrophenotriazine,  $C_6H_4<\begin{array}{l}N-CH_2\\ |\quad\ \ |\\ N-NH\end{array}$. Orthamidoazotoluene and benzaldehyde yield phenylparatolyldihydroparatolutriazine,

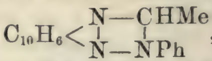


$$C_7H_6<\begin{array}{l}N-CHPh\\ |\quad\ \ |\\ N-N\cdot C_6H_4Me\end{array},$$

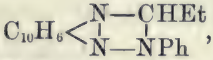
and benzeneazo-β-naphthylamine and benzaldehyde yield diphenyldihydro-β-naphthatriazine,  $C_{10}H_6<\begin{array}{l}N-CHPh\\ |\quad\ \ |\\ N-NPh\end{array}$.

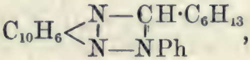
In the present paper the authors describe a series of compounds formed from benzeneazo-β-naphthylamine and orthamidoazotoluene by the action of various aldehydes, namely, formaldehyde, acetaldehyde, propaldehyde, œnanthaldehyde, and furfuraldehyde. The compounds so obtained are mostly colourless, well crystallised substances, have distinctly basic properties, give, with concentrated hydrochloric acid, well crystallised hydrochlorides which dissolve in alcohol without decomposition, but are decomposed into hydrochloric acid, and the dihydrotriazine by a large quantity of water. The hydrochlorides easily yield platinochlorides. They are not decomposed when heated with concentrated hydrochloric acid at 150° under pressure, and are not altered when boiled with stannous chloride and hydrochloric acid. The authors point out that the formation of dihydrotriazine derivatives is evidence in support of the view that the orthamidoazo-compounds are to be considered as hydrazones of orthoquinonimides.

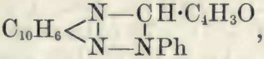
Phenyldihydro-β-naphthatriazine,  $C_{10}H_6<\begin{array}{l}N-CH_2\\ |\quad\ \ |\\ N-NPh\end{array}$, is obtained by heating benzeneazo-β-naphthylamine with alcohol and a 40 per cent. aqueous solution of formaldehyde for some hours at 140° in a sealed tube. It is better, however, to employ a slight excess of paraformaldehyde. The product is purified by crystallisation from alcohol and decolorisation with animal charcoal. It forms transparent tablets, melts at 164°, and contains $\frac{2}{3}$ mol. of water of crystallisation. After drying at 100°, it melts at 184°, is easily soluble in alcohol, sparingly in cold benzene and ether, and insoluble in light petroleum. The *hydrochloride*, $C_{17}H_{13}N_3HCl$, is obtained by adding concentrated hydrochloric acid to an alcoholic solution of the base. It crystallises in slender, white needles, melts at 254°, is soluble in alcohol and dilute hydrochloric acid, and is decomposed by pure water. The *platinochloride*, $(C_{17}H_{13}N_3)_2,H_2PtCl_6$, is obtained as a yellow precipitate on adding platinic chloride to an alcoholic solution of the base containing hydrochloric acid; it carbonises about 240°.

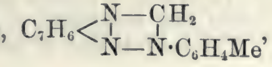
Methylphenyldihydro-β-naphthatriazine,  $C_{10}H_6<\begin{array}{l}N-CHMe\\ |\quad\ \ |\\ N-NPh\end{array}$, is obtained by adding excess of acetaldehyde to benzeneazo-β-naphthylamine suspended in alcohol. Heat is developed, and a deep-red solution is obtained in a short time. The product is purified either by crystallisation from alcohol and decolorisation with animal charcoal, or by dissolving in benzene and precipitation with petroleum. It crystallises in beautiful, colourless, rhombic tablets, is easily soluble in hot alcohol, more sparingly in benzene, and most sparingly in ether, and is insoluble in light petroleum. When heated with concentrated hydrochloric acid for some hours at 150° in a sealed tube, only the hydrochloride is formed, and the free base is regenerated on treatment with ammonia. It is unaltered when boiled with stannous chloride and hydrochloric acid in alcoholic solution. The *hydrochloride*, $C_{16}H_{15}N_3,HCl$, forms beautiful, transparent tablets, and melts at 252°. The *platinochloride*, $(C_{16}H_{15}N_3)_2,H_2PtCl_6$, forms yellow needles which decompose at 260° with carbonisation.

Methylphenyldihydro-β-naphthatriazine methiodide, $C_{18}H_{15}N_3,MeI$, is obtained by heating the above base with methyl iodide and methyl alcohol at 100° under pressure, and purifying the product by crystallisation from alcohol. It forms transparent tablets, and melts at 244°. The iodide, when treated in alcoholic solution with freshly precipitated silver chloride is converted into chloride, and the latter yields a *platinochloride*, $(C_{18}H_{15}N_3MeCl)_2,PtCl_4$, which forms slender, yellow needles, and melts at 260°.

Ethylphenyldihydro-β-naphthatriazine,  $C_{10}H_6 < \begin{array}{l} N—CHEt \\ \mid \quad\;\; \mid \\ N—NPh \end{array}$, is obtained in a manner similar to the preceding methyl compound by employing propaldehyde in place of acetaldehyde. It crystallises in slender, white needles, melts at 219°, and is easily soluble in alcohol and hot benzene, sparingly in ether, and insoluble in light petroleum. The *hydrochloride* crystallises in beautiful, white needles, and melts at 258°. The *platinochloride* forms small, yellow crystals, and carbonises about 265°.

Hexylphenyldihydro-β-naphthatriazine,  $C_{10}H_6 < \begin{array}{l} N—CH{\cdot}C_6H_{13} \\ \mid \quad\;\; \mid \\ N—NPh \end{array}$, is obtained by heating a mixture of the amidoazo-compound and œnanthaldehyde (normal heptylaldehyde) in molecular proportion for a few hours on the water-bath. It forms slender, white needles, melts at 176·5°, and is easily soluble in alcohol and benzene. The *hydrochloride* crystallises in long, white needles, and melts at 226°. The *platinochloride* is obtained as a yellow, crystalline precipitate, and melts at 225°.

Furfurphenyldihydro-β-naphthatriazine,  $C_{10}H_6 < \begin{array}{l} N—CH{\cdot}C_4H_3O \\ \mid \quad\;\; \mid \\ N—NPh \end{array}$, is obtained in a similar way to the preceding compound. It forms slender, white needles, and melts at 241°. The *hydrochloride* crystallises in transparent tablets, and carbonises about 230°. The *platinochloride* is obtained as a bright-yellow, crystalline precipitate, and carbonises about 240°.

Paratolyldihydrotolutriazine,  $C_7H_6 < \begin{array}{l} N—CH_2 \\ \mid \quad\;\; \mid \\ N—N{\cdot}C_6H_4Me \end{array}$, is obtained by heating orthamidoazotoluene with excess of paraformaldehyde for some hours, at 140°, in a sealed tube. It crystallises in white, lustrous prisms, melts at 178°, and is easily soluble in hot alcohol, sparingly soluble in ether. The *hydrochloride* crystallises in white tablets, and melts at 220°. The *platinochloride* is obtained as a yellow, microcrystalline precipitate, and melts at 216°.

Ethylparatolyldihydrotolutriazine is obtained by heating a mixture of propaldehyde and orthamidoazotoluene at 140°. It crystallises from hot benzene in white needles, and melts at 168°. The *hydrochloride* forms long, white needles, and melts at 96°. The *platinochloride* forms small, yellow needles, and melts at 221°.

Hexylparatolyldihydrotolutriazine is obtained by heating orthamidoazotoluene with œnanthaldehyde for several hours, at 175°, in a sealed tube. It forms slender, white needles, and melts at 165°. The *hydrochloride* forms transparent tablets, and melts at 96°. The *platinochloride* is obtained as a yellow, crystalline precipitate, and melts at 171°.
E. C. R.

Sparteïne. By F. B. Ahrens (*Ber.*, **24**, 1095—1097).—*Oxysparteïne*, $C_{15}H_{24}N_2O$, prepared by the oxidation of sparteïne, is purified by means of the platinochloride; it crystallises from ether in colourless, hygroscopic needles, melts at 83—84°, and is readily soluble in alcohol, chloroform, or water. The *hydrochloride*,

$$C_{15}H_{24}N_2O,2HCl + (?)\ H_2O,$$

is obtained from water in large, broad needles, and melts at 48—50°. The *hydrobromide* is also crystalline; the *sulphate* is readily soluble, and crystallises in slender, lustrous needles. On the addition of platinic chloride to a dilute solution of the hydrochloride, lustrous, ruby-coloured crystals are deposited which have the formula $(C_{15}H_{24}N_2O)_2,PtCl_4 + 4H_2O$, and melt at 209° with decomposition From the mother liquors, on evaporation, needle-shaped crystals of the *normal salt*, $C_{15}H_{24}N_2O,H_2PtCl_6 + 2H_2O$, are formed; this melts at 221—223° with decomposition. The *aurochloride*, $C_{15}H_{24}N_2O,HAuCl_4$, crystallises from water in lustrous needles or plates, softens at about 163°, and decomposes at about 186°. The corresponding *mercury* compound is crystalline; it softens at 52°, and melts at 57—58°. The *picrate* crystallises in long, lustrous needles, and melts at 176—178°.
J. B. T.

Alkaloïds from the Seeds of Delphinium staphisagria, L. By Charalampi (*J. Pharm.* [5], **23**, 302—306; from *Pharm. Zeit. Russ.*, **29**, 641).—To extract these alkaloïds, 2 kilos. of the seeds is digested in 8 kilos. of 80 per cent. alcohol during four days at 15°. The liquid is removed, and the residue is again treated until the extraction is complete. The alcohol is evaporated below 60° under diminished pressure and the residue from the distillation is diluted with an equal volume of water. After 24 hours, three layers are formed: an upper one of a greenish, fatty oil; a middle one of brown, aqueous, alcoholic liquid; and a lower one composed of a resinous mass. The lower layer is run off. The middle one is freed from alcohol at a temperature not exceeding 50°. The oily layer, which retains a considerable amount of alkaloïds, is agitated with water containing a little sulphuric acid, allowed to remain five or six days, the layers formed separated, and the oily part again repeatedly treated (10 times). The acid liquids are united, filtered, treated with ether to remove the last traces of fat, and united with the liquid obtained from the aqueous alcoholic layer. Hydrogen sodium carbonate is added, and then ether to take up the alkaloïds. The ethereal solution is removed and evaporated, spontaneously towards the end, when delphinine is not long in making its appearance on the sides of the vessel. This base is purified by combining it with tartaric acid, and repeating the treatment with hydrogen sodium carbonate and ether.

Delphinine has the formula $C_{62}H_{49}NO_{14}$, as deduced from direct analysis, and also from the composition of its aurochloride and platinochloride; this differs sensibly from the composition given by Dragendorff and Marquis, in 1877. It gives anhydrous, rhombic crystals. It withstands a temperature of 120°, but a little higher it begins to colour, and melts at 191·8°. It has a pungent, burning taste. 1 gram dissolves at 15° in 20·49 grams of benzene, in 642·4 grams of light petroleum (sp. gr. 0·633) in 53·4 grams of ether of 0·728 sp. gr., in 47·6 grams of absolute ether, in 44·4 grams of absolute alcohol, in 238 grams of 90 per cent. alcohol, and in 1594 grams of water. The recently prepared aqueous solution has an alkaline reaction. This base gives crystallisable salts with nitric and sulphuric acids sparingly soluble in water, alcohol, and ether; they easily dissolve in acidified water. Hydrochloric, acetic, oxalic, and tartaric acids yielded amorphous compounds.

The mother liquor, left after removal of the delphinine, when evaporated very slowly, yields a certain quantity of *delphisine*, $C_{62}H_{50}NO_{14}$, in the form of acicular crystals melting at 189·2°. This alkaloïd dissolves at 15° in 75·2 parts of benzene, in 665 of light petroleum, in 43 of ether of sp. gr. 0·728, in 71 parts of absolute ether, in 104 of 90 per cent. alcohol, and in 370 parts of absolute alcohol. It is very slightly soluble in water, but dissolves readily in chloroform, as does delphinine.

Delphinoïdine, $C_{50}H_{42}NO_8$, obtained in an amorphous state after the foregoing, is scarcely soluble in water; at 15°, 1 part dissolves in 9·43 parts of light petroleum, in 30·5 of benzene, in 17·8 of 90 per cent. alcohol, in 4·03 of ether (sp. gr. 0·728), and in 37·03 of absolute ether. The author has also examined the product previously described as staphisagrine, which forms the residue of the operations yielding the alkaloïds already described. This base appears to him to be really a mixture of four amorphous alkaloïds. Delphinine, delphisine, and delphinoïdine, especially the two former, are highly poisonous, resembling aconitine in their action. J. T.

Alkaloïds of the Roots of Sanguinaria canadensis and Chelidonium majus. By G. König (*Chem. Centr.*, 1891, i, 321—322; from *Zeit. Naturwiss. Halle*, **63**, 369—426).—The roots of *Sanguinaria canadensis*, a native of North America, and the sanguinarine of commerce contain several alkaloïds, including *chel-*

erythrine, which is present in greatest quantity, *sanguinarine*, *γ-homochelidonine*, and *protopine.*

Chelerythrine crystallises with a molecule of alcohol, which is not separated at a temperature of 150°; the formula is $C_{21}H_{17}NO_4 + C_2H_6O$; melting point 203°. It is identical with the alkaloïd which the author separated from the celandine, *Chelidonium majus.* The *aurochloride*, $C_{21}H_{17}NO_4,HAuCl_4$, melts at 233°; the *platinochloride* is $(C_{21}H_{17}NO_4)_2,H_2PtCl_6$; the *hydrochloride* crystallises out of aqueous solution with 5 mols. H_2O, and from alcohol with 4 mols. H_2O. The salts are lemon-yellow.

Sanguinarine, $C_{20}H_{15}NO_4$, is very similar to chelerythrine in its properties; it crystallises with ½ mol. H_2O, and melts at 211°; its salts are red. The *hydrochloride*, $C_{20}H_{15}NO_4,HCl + 5H_2O$, the *nitrate*, $C_{20}H_{15}NO_4,HNO_3 + H_2O$, the *aurochloride*, $C_{20}H_{15}NO_4,HAuCl_4$, and the *platinochloride*, $(C_{20}H_{15}NO_4)_2,H_2PtCl_6$, were prepared.

The base which the author has named *γ-homochelidonine* is probably identical with that separated by Selle from *Chelidonium majus*, and its formula is probably $C_{22}H_{21}NO_4$. Its behaviour with alkaloïd reagents resembles that of Selle's γ-homochelidonine. The fourth alkaloïd, *protopine*, was prepared from *Chelidonium majus*, *Sanguinaria canadensis*, and from opium, all the three specimens being identical. Its formula is $C_{20}H_{17}NO_5$, and it melts at 204°; the *platinochloride*, $(C_{20}H_{17}NO_5)_2,H_2PtCl_6 + 3H_2O$; and the *aurochloride*,

$$C_{20}H_{17}NO_5,HAuCl_4,$$

melting at 182°, were prepared; the *hydrochloride*, $C_{20}H_{17}NO_5,HCl$, crystallises in two different forms, and appears to be free from combined water. J. W. L.

Alkaloïds of Sabadilla Seeds. By E. MERCK (*Chem. Centr.*, 1891, i, 363).—The author has isolated two alkaloïds from sabadilla seeds, *Asagrœa officinalis.* *Sabadine* is best separated as the nitrate. It has the formula $C_{29}H_{51}NO_8$, melts at 238—240° with decomposition, and is readily soluble in alcohol and ether, sparingly soluble in light petroleum. With concentrated sulphuric acid, a yellowish coloration is at first produced, showing a green fluorescence, which gradually changes to blood-red and finally to violet. The alkaloïd attacks the mucous membrane of the nose and causes sneezing. The *hydrochloride* crystallises with 2 mols. H_2O, which it loses at 101°; it melts at 282—284° with decomposition. The *hydrobromide*, the *nitrate*, and the *aurochloride* were analysed.

Sabadinine, $C_{27}H_{45}NO_8$, the second alkaloïd, does not melt at any definite temperature. It is separated from the sulphate by soda solution, and extracted with chloroform. With concentrated sulphuric acid, a permanent blood-red coloration is produced. It does not irritate the nasal mucous membrane. The sulphate crystallises with 2½ mols. H_2O. Neither sabadine nor sabadinine is precipitated from the solution of its salts by the addition of caustic alkalis, alkaline carbonates, or ammonia in the cold, it being necessary to warm the solution, when the alkaloïd is precipitated in flakes. J. W. L.

Ptomaïnes. By O. DE CONINCK (*Compt. rend.*, **112**, 584—585).—The ptomaïne $C_{10}H_{15}N$ (Abstr., 1890, 1170) yields a *hydrobromide* crystallising in white needles, which become rose-coloured when exposed to air. It is deliquescent, very soluble in water, less soluble in strong alcohol, and almost insoluble in pure ether. The same precautions must be observed when preparing this compound as in the preparation of the hydrochloride (*loc. cit.*). The *modified platinochloride*, $(C_{10}H_{15}N)_2,PtCl_4$, should be prepared with tepid water that has previously been boiled. It forms pale-brown plates, insoluble in cold water, soluble in hot water, but decomposed if ebullition is prolonged. It melts at about 206°, and is stable in moist air, differing in this respect from the normal platinochloride. The *aurochloride*, $C_{10}H_{15}N,HAuCl_4$, is a pale-yellow compound, insoluble in cold water, soluble in warm water, and decomposed by boiling water. It is somewhat stable in moist air. With alcoholic potash, the methiodide of the ptomaïne gives, when heated, an immediate bright-red colour, which rapidly changes to brown, and after some time acquires a persistent greenish-blue fluorescence. C. H. B.

Vegetable Hæmatin. By T. L. PHIPSON (*Compt. rend.*, **112**, 666—667).—The vegetable hæmatin obtained by Linossier from *Aspergillus niger* (this vol., p. 751) is in all probability identical with the *palmelline* obtained by the author in 1879 from *Palmella cruenta*.

Palmella cruenta, which was formerly called *Chaos sanguinea*, is sometimes found completely green in the neighbourhood of London, and becomes blood-red towards the end of vegetation. In this connection it is noteworthy that biliverdin has a green colour very similar to that of chlorophyll, and gives a definite absorption spectrum. C. H. B.

Physiological Chemistry.

Hæmoglobin. By M. SIEGFRIED (*Chem. Centr.*, 1891, i, 228—229).—Schützenberger's indigo-carmine method of estimating oxygen in blood is stated to give a higher result than that with the air-pump. In the present research, operations were performed in an atmosphere of hydrogen. The result was that with defibrinated dog's blood, the percentage of oxygen found by the air-pump was 16·1 per cent.; and by Schützenberger's method 7·6—7·9 per cent. This difference is put down to one of the two following factors: either the blood spectrum which shows the bands of reduced hæmoglobin is untrustworthy, and the blood still contains a good deal of oxygen; or else the titration with the hyposulphite solution was incorrect. The former alternative is decided on, and the term pseudohæmoglobin is applied to the supposed compound of oxygen with hæmoglobin which shows the band of reduced hæmoglobin. W. D. H.

Myelin. By J. Gad and J. F. Heymans (*Chem. Centr.*, 1891, i, 230).—The name myelin is applied to the white substance sheathing nerve-fibres, and stated to contain proteïds, extractives, neurokeratin, lecithin, protagon, cerebrin, and cholesterol. This sheath, moreover, is stained black by osmic acid. The present research is directed to determining more exactly what myelin is. The characteristic properties of myelin are believed to be due to lecithin, either free or only loosely combined, because lecithin elsewhere, for instance, in nerve-cells, where it is probably more firmly combined, does not show the characters of myelin.

Nerve-fibres are divided into groups corresponding to the presence or absence of myelin in their sheaths. W. D. H.

Influence of Carbohydrates on Proteïd Metabolism. By G. Lusk (*Zeit. Biol.*, **27**, 459—481).—The influence on proteïd metabolism of carbohydrates taken as diet, or circulating abnormally in the system in diabetes, is of some pathological importance. Cases of diabetes not, however, being forthcoming, certain experiments bearing on the subject were undertaken by the experimenter on his own person.

Two double series of observations were made, each lasting two or three days, and the general results may be stated in the following tabular form :—

Experiment.	Daily averages.			
	Food.		Nitrogen excreted.	Difference between N ingested and N excreted.
	Nitrogen.	Carbohydrate.		
1*a*	20·549	357·37	19·837	+0·712
1*b*	20·549	10·8	25·930	−5·381
2*a*	9·230	347·8	13·785	−4·555
2*b*	9·230	2·8	15·807	−6·577

In both cases, it is seen that the absence of carbohydrate food increases the proteïd waste in the tissue, the carbohydrate protecting a certain amount of proteïd from destruction. Further experiments showed that the amount of fat undergoing combustion was increased during deprivation of carbohydrate.

There can be no doubt, therefore, that in diabetes the upsetting of the metabolic balance is due to the non-destruction and the consequent separation in the urine of a large quantity of sugar, which under normal circumstances would have undergone combustion and saved much proteïd and fat from destruction. The increase of oxygen consumed and carbonic anhydride given off would not, however, be markedly different from that observable in a healthy person under similar circumstances; the total amount would, however, probably be less, as the diabetic would, other things being equal, weigh less than the healthy person. W. D. H.

Muscular Work and the Excretion of Urea. By I. Munk (*Chem. Centr.*, 1891, i, 230—231).—The work of Argutinsky on this subject is criticised, and the older opinion that moderate work does not increase the excretion of urea upheld (compare this vol., p. 596). W. D. H.

Inorganic Constituents of Bone and Organs of Normal and Rachitic Children. By H. Brubaker (*Zeit. Biol.*, **27**, 517—549).—The bodies of three healthy children were investigated in reference to the inorganic constituents, and especially the calcium, in the bones and other organs. The three subjects of analysis were aged, 28 weeks' fœtus, new-born child, and 4 years respectively, and very full tables of analyses are given. The following general results were obtained :—

(1.) The skeleton (as was formerly shown by E. Voit) becomes poorer in water as age progresses, and richer in ash and in the chief constituents of the ash.

(2.) The amount of water in soft parts similarly diminishes with age. The constituents insoluble in water, like chalk and iron, diminish, the phosphoric acid increasing. This is different from what Voit found in dogs.

(3.) Cartilage and spongy bone are in these particulars like the soft parts.

(4.) The increase of ash in the bones more than compensates for the diminution in other parts, so that the ash of the whole body increases with age up to a certain maximum.

The following selections from the tables illustrate the foregoing points :—

Bone (Three Healthy Children).

Constituents.	In 100 parts.			In 100 parts dry fat-free bone.			In 100 parts ash.		
	1.	2.	3.	1.	2.	3.	1.	2.	3.
Water	72·2	—	45·0	—	—	—	—	—	—
Fat	0·6	—	2·5	—	—	—	—	—	—
Ash	11·3	—	27·9	41·5	48·8	53·2	—	—	—
CaO	5·4	—	15·0	19·9	23·9	28·6	48 0	48·9	53·8
MgO	0·16	—	0·4	0 6	0 6	0·8	1·4	1·3	1 6
P_2O_5	4·5	—	11·9	16·7	19·8	22·6	40·2	40·7	42·6

The bodies of five rachitic children were then investigated in much the same way. These were also of different ages. It was found that the diminution of calcium salts occurred in the bones and not in the soft tissues, and the general conclusion is drawn that the administration of calcium salts would not in the greater number of cases of rickets be of any avail.

Muscles (Healthy Children).

Constituents.	In 100 parts.			In 100 parts of dry fat-free organ.			In 100 parts of ash.		
	1.	2.	3.	1.	2.	3.	1.	2.	3.
Water	83·9	—	77·2	—	—	—	—	—	—
Fat...........	2·2	—	1·8	—	—	—	—	—	—
Ash	1·0	—	1·0	7·5	6·4	5·3	—	—	—
CaO	0·03	—	0·01	0·2	0·2	0·04	2·8	3·1	0·82
MgO	3·02	—	0·02	0·1	0·1	0·1	1·9	2·1	2·2
P_2O_5	0·3	—	—	1·9	1·5	2·0	28·7	23·6	37·9
Fe_2O_3	0·01	—	0·01	0·1	0·1	0·04	1·16	1·4	0·7

The following analyses of two of these cases, the ages of which agree pretty well with those of the healthy subjects investigated, may be quoted :—

Bone (Rachitic Children).

Constituents.	In 100 parts.		In 100 parts of dry fat-free bone.		In 100 parts of ash.	
	A. 8 mths. fœtus.	D., aged 3 yr. 8 m.	A.	D.	A.	D.
Water	79·3	73·2	—	—	—	—
Fat	0·5	0·5	—	—	—	—
Ash	6·38	6·2	31·6	13·52	—	—
CaO......	2·5	2·7	12·4	10·4	39·2	44·2
MgO	0·04	0·04	0·2	0·1	0·7	0·5
P_2O_5	2·16	1·97	10·7	7·5	33·8	31·8

W. D. H.

The Influence of Acid Mineral Salts on the Composition of Bones. By H. WEISKE (*Landw. Versuchs-Stat.*, **39**, 17—30).—Experiments were made on rabbits by adding sodium hydrogen phosphate to their food, to ascertain if mineral matter was removed from the skeleton; but the results were unsatisfactory; the differences between the composition of the normal bones and that of those animals which had not received phosphate were too slight to indicate any real change. The urine was always found to be alkaline, whilst in experiments previously made with free acid, the urine had been neutral, or slightly acid. Possibly larger doses of acid phosphate might have the desired effect. E. W. P.

Iron in the Liver and Spleen. By F. KRÜGER, C. MEYER, and M. PERNOŬ (*Zeit. Biol.*, **27**, 439—458).—The importance of estimations of iron in the liver and spleen has been, during recent years, increased, as it has been shown by Quincke and others that in pernicious anæmia the amount normally present is much increased. Comparatively few observations have, however, hitherto been made on the relative amount of the metal at different ages, and the present communication relates to this point. The animals, the organs of which were investigated, were calves, cows, and oxen, and also human fœtuses of various ages. The present paper contains references to former work on the subject, tables of analyses performed in the present research, and the following general conclusions :—

1. The amount of iron in the liver cells of the fœtus is very much higher, in the mean, 10 times higher, than that in adults. Care was taken in these experiments, as also in those with the cells of the spleen, to obtain the cellular elements, after crushing the organ completely, free from hæmoglobin and other impurities by carefully washing with salt solution (0·6 per cent.) and the use of the centrifugal machine. It was found that, although the saline solution dissolves out a small quantity of proteïd matter from the cells, it does not remove from them any iron-containing constituents.

2. The iron of fœtal liver cells differs in amount at different stages of development. It begins to increase markedly about the end of the first half of pregnancy, reaches a maximum, then falls, and rising, reaches a second maximum three or four weeks before birth. From then until four weeks after birth, it sinks in amount until it is nearly normal.

3. In calves, it was found that for the first week after birth the iron is seven times more abundant in the liver than in the adult animal; it reaches the adult standard in about four or six weeks.

4. The amount of iron in the liver of adult animals shows very slight variations, and no noteworthy difference in the amount in the liver of cows and oxen was found.

5. The splenic cells of the fœtus are poor in iron as compared with those of the adult. The amount of iron in them begins to increase after birth, reaching the normal in about two months.

6. Although there is no difference in the amount of iron contained in the splenic cells of pregnant and non-pregnant cows, it is five times greater than that in the splenic cells of the ox.

7. The amount of iron in the spleen of adult animals, especially females, undergoes greater changes than that in calves or fœtuses.

W. D. H.

Composition of Butter Fats. By W. JOHNSTONE (*Chem. News*, **63**, 56).—The author states that butter fat contains neither stearin nor normal oleïc acid; but that it consists of a mixture of glyceryl "isoleate-palmitate-caprate" and "tri-nondecatoate" in varying proportions. In some butter fats, the radicle of œnanthoic acid replaces one of the nondecatoic groups in the triglyceride, and forms glyceryl "dinondecatoate-œnanthoate."

G. T. M.

Human Lymph and Chyle. By I. MUNK and A. ROSENSTEIN (*Virchow's Archiv*, **123**, 484—518).—The present paper is a continuation of one already published (this vol., p. 755). Amyl oleate was administered to a patient suffering from a lymphatic fistula; during the 12 hours following its administration, 26 per cent. of the fat given was recovered in the chyle, in the form of oleïn, the synthesis of oleïc acid with glycerol having occurred in the process of absorption. No amyl alcohol was found in the chyle. Artificial digestion experiments showed that pancreatic juice has the power of splitting amyl oleate into amyl alcohol and oleïc acid.

Charcoal, in a fine state of subdivision, was next given, with the view of ascertaining whether fine particles as small as or smaller than the oil globules of an emulsion are taken up in the same way. But the lymph was entirely free from them, showing, as has been previously stated, that absorption of fine solid particles does not occur.

Is oil absorbed from the rectum? was the next point investigated; after injection of oleïn into the rectum, it was found that from 3·7 to 5·5 per cent. of the fat given appeared in the chyle.

Similar experiments were then undertaken to determine whether proteïd and sugar (given in large doses) appear in the chyle after being administered as food. It was found that the administration of proteïd, as of any food, increases the flow of lymph, but that its percentage of proteïd does not rise. On the other hand, the sugar in the chyle is increased, and after a large quantity of sugar as food, the percentage in the chyle may be doubled as compared with the amount during inanition (compare Ginsberg, Abstr., 1890, 276).

The paper concludes with further analytical data respecting the solid constituents and inorganic salts of the chyle and lymph. The composition of the lymph ash was as follows:—In 100 parts of lymph, 0·8675 part of ash was obtained; in 100 parts of the ash, the following numbers give the percentages of its different constituents:— $NaCl$, 67·0; Na_2CO_3, 24·9; K_2HPO_4, 3·2; $Ca_3(PO_4)_2$, 3·2; $Mg_3(PO_4)_2$, 1·1; $Fe(PO_4)_2$, 0·3.

Further, it was found that lymph and chyle contain an amylolytic ferment; but that neither contains a sugar-destroying ferment as stated by Lépine. W. D. H.

Indigo-red (Indirubin) in Urine. By H. ROSIN (*Virchow's Archiv*, **123**, 519—566).—Many red pigments under different names have been described in normal, and more particularly in morbid, urines. One of these appears to be indirubin or indigo-red, although its absolute identification with the indigo-red obtained from plants has not, hitherto, been thoroughly worked out. The imperfect data given by various workers on urinary pigments render it also desirable that those which are, and those which are not, identical with indigo-red should be accurately determined.

Indigo-red was prepared artificially from commercial indigo; it was also prepared by a modification of Berzelius' method from the indican of plants, and also from the urine. The percentage composition, the crystalline form, and other properties, and the relation of the pigments to indigo-blue were in all cases absolutely identical.

The pigments which are identical with indigo-red are Heller's urrhodin, as Schunk first showed, Leube's pathological urinary pigment, and Plósz's urorubin. Those red pigments which are not the same as indigo-red are the scatole pigment, Nencki and Sieber's uroroseïn, which has characteristic solubilities and reactions, uroerythrin (the pigment in deposits of urates), urohæmatin, Giacosa's pigment, and urorubrohæmatin. W. D. H.

Analysis of Pathological Liquids. By G. Patein (*J. Pharm.* [5], **23**, 390—394).—From a hydrocephalous subject was taken 380 c.c. of a colourless liquid, turbid after filtration, in which some flocculent filaments appeared after being some time in repose. The reaction was alkaline, and only faint traces of albumin appeared on boiling in presence of 2 drops of acetic acid. Sp. gr. 1·004; solid residue 9·4 grams per kilo.; anhydrous salts 7·6 grams, containing sulphates, hydrogen carbonates, but no phosphates. Agitation with ether did not extract either fatty matters or cholesterol. Fehling's solution was not reduced.

Ovarian Cysts.—1. Syrupy liquid, not stringy, reddish, with pulverulent deposit. Sp. gr. 1·013; solid residue 61·5 per kilo.; anhydrous salts 7·5; chlorides 6·5; proteïd matters 54·0. No globulin was precipitated by magnesium sulphate. The liquid was coagulable by heat, but the coagulum disappeared on the least addition of acetic acid. 2. Fibrome, size of an orange, from a woman 47 years old.—The fibrome contained water 750·0 grams per kilo.; solid matters 242·0; anhydrous salts 6·2 grams, with traces of urea, cholesterol, myosin, and fats. The contents of the cyst were gelatinous, and included a notable amount of mucin; it did not coagulate either when boiled alone or with acetic acid. 3. Cyst from a woman of 38 years.—Amount of liquids 35 litres; reaction scarcely alkaline. Sp. gr. 1·004; solids 12·6 grams per kilo.; anhydrous salts 9·15; albumin 1·10. Neither globulin, fat, nor cholesterol were present. The proteïd matters were completely precipitated by heat and acetic acid. 4. Cyst from a woman of 51 years.—Amount of liquid 40 litres, alkaline, chocolate coloured, somewhat thick consistency. Sp. gr. 1·019; total solids 57·3 grams per kilo.; anhydrous salts 9·20. The proteïd substances were completely precipitated by heat and acetic acid. From these results it is evident that albumin is subject to modification, which must be considered in its detection and estimation.

The following table gives the results of analyses (in grams per kilo.) of healthy and altered tissues in cases of cancer. 1. Cancer of the breast running a very rapid course. 2. Breast cancer of recent development.

	Healthy tissue adjoining.		Tumour.		Liquid portion.
	1.	2.	1.	2.	1.
Water	175·5	476·0	830·5	849·0	928·6
Total solids	824·5	524·0	169·5	151·0	71·4
Anhydrous salts	4·2	8·5	11·5	16·4	—
Fat	considerable amount	notable amount	0·0	0·0	—
Proteïd	—	—	—	—	60·5
Globulin & mucin	—	—	—	—	traces

The liquid portion of 1 did not coagulate on boiling with 2 drops of acetic acid. A third tumour has given traces of cholesterol.

Polypes of the Nose.—These are generally of small weight, and contain a large proportion of water; their albumin may or may not coagulate when boiled with acetic acid. In a particular case, one weighed 373 milligrams with 13·37 per cent. of solids; it contained a notable amount of calcium phosphate. The presence of this compound in all nasal polypes is worthy of note.

A tumour taken from the kidney gave 1100 c.c. of liquid of a neutral reaction. Sp. gr. 1·023; total solids 118·8 grams per kilo.; anhydrous salts 7·6; chlorides 5·45. Mucin and albuminoses were present, but neither uric acid, urea, hippuric acid, fat, nor cholesterol was found. After elimination of mucin and albuminoses, the proteïd matters are not coagulated on boiling with acetic acid. It is seen that the tumour contains no element of urine. J. T.

Action of Opium and Morphine on the Intestine. By W. Spitzer (*Brit. Med. J. Epitome*, 1891, 134; from *Virchow's Archiv*, **123**, 593—628).—The experiments were carried out on rabbits, frogs, and men, their object being to increase our knowledge of the action of opium on the intestine, and to determine whether opium is better than morphine as an anti-diarrhœic and anodyne. In frogs, the bowel was exposed and kept moist with saline solution. Very small doses of aqueous extract of opium given subcutaneously sufficed to diminish the sensitiveness of the bowel to painful stimuli, whilst leaving intact the sensitiveness to stimuli which excite peristalsis. The sensitiveness of the skin was also not affected, nor was there any general narcosis. The conclusion is drawn that the action of opium cannot under these circumstances be on the brain, as the same result is obtained with headless frogs; nor on the spinal cord, as its other functions are intact, but on the bowel locally. The local action of opium was also shown by giving a frog strychnine; then tying the intestine midway between the stomach and anus, opium was injected into the lower half, and its power of calling forth convulsions on stimulation was then markedly diminished. The opinion is held that opium paralyses not the sensory endings, but sensory ganglia on the course of the sensory nerves in the wall of the canal. The motor ganglia are not so readily affected, larger doses being necessary to lessen peristalsis.

The diminution of peristalsis may be due to paralysis of motor ganglia in the bowel, or to a stimulation of the inhibitory centres in the cord from which the splanchnic nerves arise. Paralysis of the sensory nerve terminations in the wall of the intestine does not occur, because after very large doses of morphine the peristaltic movements of the bowel become very marked, and experiments pointed to the conclusion that the diminution in peristalsis was very largely due to an action of the opium in paralysing the motor ganglia in the walls of the intestinal canal. Large doses caused great increase of bowel peristalsis before general spinal tetanus was induced. This is probably due to paralysis of the spinal cord, and consequent paralysis of the inhibitory action exerted by the splanchnic nerves. In this condition, however, the sensitiveness of the intestine to painful stimuli is much diminished. Morphine has the same action in every way, and quantitatively the activity of the opium is proportional to the amount of morphine it contains. The other alkaloïds of opium have very little action on the bowel. On rabbits, observations were made after exposing the bowel while the animal lay in a warm bath of saline solution. The experiments of Nothnagel are confirmed, in which he found that irritation of the bowel with sodium chloride is not nearly so effectual in increasing peristalsis after the administration of opium or morphine. If a portion of bowel be completely isolated and the same experiment repeated, then peristalsis is not interfered with; this result is regarded as proving that in this case the opium acts on the spinal cord, and diminishes the inhibitory action of the splanchnic nerves. It is, however, pointed out that irritation of the bowel from without with sodium chloride scarcely corresponds with physiological peristalsis or increased peristalsis after purgatives or irritation from within of the mucous membrane, as the peristalsis takes place towards the pylorus, and is very inconstant in amount. The bowel was therefore irritated by injecting into it a 15 per cent. salt solution, coloured with indigo-carmine. The rate at which this solution progressed down the intestine was observed in normal animals, and was found to be two or three times slower after opium or morphine, the peristalsis being also much more gentle and regular in the latter case. Even after complete isolation of a portion of the intestinal canal from its mesenteric nerves, opium greatly diminishes the peristalsis. Opium given subcutaneously acts exactly to the same extent, and no better than, morphine subcutaneously, its activity being proportional to the amount of morphine it contains. In healthy men, opium by the mouth acts somewhat more powerfully on the bowel than when given subcutaneously. The reason, probably, is that the morphine is only slowly abstracted from the opium, and thus acts gently along the whole length of the bowel; it is not so quickly absorbed as pure morphine is, and in consequence does not produce so marked a general action. In diarrhœa, opium by the mouth is more powerful than opium extract or morphine subcutaneously, or morphine by the mouth. In slight intestinal pain, opium by the mouth is the best treatment, as we get the desired analgesia with small doses and without constitutional effect, the local action on the bowel being probably sufficient; in very severe pain, hypodermic injection of morphine is most effectual.

W. D. H.

Poisoning by Aniline, Chlorates, and Mercuric Chloride. By W. Falkenberg (*Virchow's Archiv*, **123**, 567—602).—Silbermann (*Zeit. klin. Med.*, **11**, Heft 5 and 6; *Deutsch. med. Wochensch.*, **14**, No. 25) has stated that pyrogallol, glycerol, and potassium or sodium chlorate produce not only hæmoglobinuria (or methæmoglobinuria), but that death ensues from intravascular coagulation, set up presumably by the liberation of fibrin ferment from the disintegrated corpuscles. The situation of the clots produced is described, and the term "capillary thrombosis" is in the present paper criticised, it being so difficult to say with certainty whether the blood in the capillaries is coagulated or not during life. Further criticisms are passed on other points. Silbermann extended a few observations, followed by similar results, to other drugs, aniline, toluylenediamine, arsenic, phosphorus, and Kaufmann states the same is true for corrosive sublimate.

The present paper is largely polemical, but also describes numerous experiments with aniline, sodium chlorate, and corrosive sublimate. In respect to these poisons at least, the cause of death was not intravascular coagulation. The blood, on the contrary, had less tendency than normal to coagulate. W. D. H.

Physiological Action of Lupetidine and Allied Substances in Relation to their Chemical Constitution. By A. Gürber (*Chem. Centr.*, 1891, **1**, 232—235).—The series of substances, copellidine, parpevoline, propyllupetidine, isobutyllupetidine, and hexyllupetidine have for their nucleus piperidine, of which lupetidine is a dimethyl substitution product; and if the hydrogen atom adjacent to the nitrogen atom is replaced by methyl, ethyl, &c., further members of the group are obtained. Small doses of these substances were administered to animals. The intensity of their action (paralysis of the voluntary muscles) may be compared by the following numbers: lupetidine, 50; copellidine, 100; parpevoline, 200; hexyllupetidine, 200; isobutyllupetidine, 250; propyllupetidine, 400. The actual seat of paralysis, whether central or peripheral, was not definitely determined. The intensity of the action is proportional to the number of methyl groups present in the molecule. W. D. H.

Use of Liquefied Carbonic Anhydride for the Rapid Filtration and Sterilisation of Organic Liquids. By A. d'Arsonval (*Compt. rend.*, **112**, 667—669).—A long cylindrical copper or steel tube containing a biscuit porcelain Pasteur-Chamberland filter is connected with a cylinder containing liquid carbonic anhydride. The gas not only drives the liquid through the filter, but under the high pressure, especially if its action is prolonged and the liquid is heated to 40°, it exerts a very powerful bactericidal and sterilising effect. The richness of the filtrate in colloïds increases with the pressure, and by varying the pressure it is possible to obtain from one and the same liquid (*e.g.*, pancreatic juice) filtrates having very different properties. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Alcoholic Fermentation and the Conversion of Alcohol into Aldehyde by the "Champignon du Muguet." By G. Linossier and G. Roux (*Bull. Soc. Chim.* [3], **4**, 697—706; see also Abstr., 1890, 1179).—Contradictory statements have been made by previous authors as to the character of the fermentation induced by the "Champignon du muguet" (a fungus producing the disease "thrush" in the mouth). Sterilised solutions inoculated with the pure fungus yield alcohol, the maximum amounts obtained being 2·7 per cent. in 43 days, using dextrose solution (*plus* necessary salts); and 5·5 per cent. in 124 days, using wort from dried raisins.

Three stages may be distinguished during the fermentation :—(1) rapid growth of the organism; (2) active fermentation; (3) lessened activity due to the toxic influence of the fermentation products, aldehyde having, it would seem, the greatest effect. "Muguet" can cause the fermentation of dextrose, levulose, and maltose; saccharose is neither inverted nor fermented, but serves as a food material; lactose cannot even be used as food. Substances other than sugars, although unfermentable, can support the growth of this fungus; such food materials, in order of nutritive value, are, dextrin, mannitol, alcohol, sodium lactate, lactic acid, gum, and glycerol; tartaric acid and tartrates barely serve to sustain life; starch, erythrol, acetic acid, acetates, oxalic acid, oxalates, aldehyde, acetone, and aromatic substances are not foods.

The sugar present is never wholly fermented by this organism, neither are the various sugars attacked at the same rate. In a mixture of equal proportions of dextrose and levulose, the ratio dextrose/levulose tends towards a minimum (0·3); hence, it is impossible to use the fungus as a means for obtaining pure levulose.

The growth of the organism is favoured by the alkalinity of the solution employed; more of the sugar is then used up, but the ratio of alcohol produced to sugar used is lowered. In addition to glycerol and succinic acid, considerable quantities of acetic acid and acetaldehyde are produced. The ordinary ferments give for the ratio glucose destroyed/acetic acid produced, a mean value 0·0025; this quantity is 0·09 to 0·14 for muguet. The aldehyde is mainly produced by the oxidation of the alcohol induced in presence of air by the ferment. A small proportion of the acetic acid present is a true excretory product of the organism, but the greater part is undoubtedly produced by the oxidation of the aldehyde without the intervention of the ferment, for muguet does not grow in an aldehyde solution. In the slowness with which fermentation takes place, in the maximum concentration of alcohol produced, and in the ratio of weight of sugar destroyed to weight of organism produced, the "Champignon du muguet" exhibits marked analogies with the *Mucorini*, and differs considerably from the *Saccharomycetes*. The conclusion that the organism does not belong to the latter is borne out by the results of a careful morphological study. W. T.

Assimilation of Nitrogen by Plants. By B. Frank and R. Otto (*Chem. Centr.*, 1891, i, 332—333; from *Ber. deut. bot. Gess.*, **8**, 331—342).—The authors have endeavoured to prove experimentally whether the Leguminosæ directly absorb pure nitrogen by means of the leaves or not, and to this end experiments have been made with cut leaves. So far, however, the results obtained are not sufficiently definite.

Experiments on the growth of the rhizobium of the root nodules in the presence of the organism of the nodules in solutions containing (*a*) sugar, (*b*) sugar and asparagine, (*c*) asparagine, show that the growth was most rapid in the presence of both sugar and asparagine, and least rapid when sugar alone was supplied.

Finally, peas were grown in unsterilised earth, in sterilised earth, and in sterilised earth to which a small quantity of the fresh soil was added. All the plants grew perfectly, and assimilation of nitrogen took place in every case. J. W. L.

Simultaneous Evolution of Oxygen and Carbonic Anhydride by Cactæ. By E. Aubert (*Compt. rend.*, **112**, 674—676).—Cactæ, when exposed to light of moderate intensity at a temperature of 35°, evolve oxygen and carbonic anhydride, their respiration ratios being 0·98 (*Opuntia*) to 0·88 (*Mamillaria*), whilst their assimilation ratios are 2·38 to 2·28. This result is probably due to the fact that the thin superficial chlorophyllian layer is not able to decompose the whole of the carbonic anhydride evolved by respiration from the colourless parenchyma underneath. The intense light of the tropics decomposes the whole of the carbonic anhydride, and in the tropics loss of carbon takes place only during the night. C. H. B.

Influence of Salt on the Formation of Starch in Vegetable Organs containing Chlorophyll. By P. Lesage (*Compt. rend.*, **112**, 672—673).—The examination of the leaves of plants growing on the sea shore, and experiments made by watering plants with pure water and with salt solutions of various strengths, show that salt has a distinct influence on the formation of starch in the chlorophyllian organs of plants, and in extreme cases prevents it. The necessary result is a decrease in the assimilation of carbon. The author has previously shown that salt reduces the quantity of chlorophyll.

C. H. B.

Presence and Function of Diastase in Plants. By J. Wortmann (*Ann. Agron.*, **17**, 84—89; from *Bot. Zeit.*, 1890, Nos. 37—41).—After a variety of experiments, the author concludes that diastase in plants has not the importance which has been ascribed to it, and that starch is transformed into soluble products by other means, probably by the agency of living protoplasm. Diastase is formed in small quantities, certainly, in leaves which contain no starch; the quantity of diastase present is in no case proportional to the amount of starch; from some starch-containing leaves, it is quite absent, and yet these leaves are the seat of very active starch-transformation. It is in special cases only, such as the germination of seeds, tubercles, and rhizomes containing starch that the solution of the starch is accomplished by diastase. The author points out that in testing for the disappearance of starch under the action of diastase the result is conclusive only when the liquid gives no blue colour with iodine after being boiled and cooled. J. M. H. M.

Formation of Nitrogenous Organic Bases by the Decomposition of Proteïds in the Vegetable Organism. By E. Schulze (*Ber.*, **24**, 1098—1101).—When the seeds of *Lupinus luteus*, *Soja hispida*, and *Cucurbita pepo* are allowed to vegetate in the dark for 12—14 days and the shoots extracted with water, a solution is obtained which, after removing proteïds as completely as possible, yields a precipitate with phosphotungstic acid. This contains considerable quantities of nitrogen, and, on treatment with milk of lime, yields nitrogenous organic bases. From *Lupinus luteus* and *Cucurbita pepo*, the author has been able to isolate the arginine described by Schultz and Steiger (Abstr., 1886, 725), whilst *Soja hispida* yields a base which is either identical with or very closely allied to arginine. The quantity of arginine obtained from *Cucurbita pepo* is small, but *Lupinus luteus* yields it in such quantities that the author has been able to show by quantitative experiments that it must have been formed at the cost of the proteïds present as reserve substance in the cotyledon.

Arginine only differs from the lysatine described by Dreschsel, inasmuch as it contains an additional atom of nitrogen and of hydrogen in the molecule. Experiments are in progress to determine, if possible, the relation existing between them. H. G. C.

Physiological Importance of Calcium Oxalate in Plants. By KOHL (*Ann. Agron.*, **17**, 90—91).—The author adds some observations to his previous work on this subject (Abstr., 1890, 191). He shares with Palladin the theory that this salt is eliminated as an accessory during the synthesis of proteïds from amides and carbohydrates. If this be true, oxalates should be found in all plants. The author shows that in many cases amongst algæ and fungi, even where little or no calcium oxalate is found, oxalic acid or soluble oxalates are still present, and diffuse rapidly out of the plant, so that a calcium salt gives a precipitate in the vicinity of many fungi, and the hyphæ of some of them are encrusted on the outside by crystals of calcium oxalate formed from the lime in the soil. Amongst fungi forming oxalic acid in large quantities the author notes *Saccharomyces Hansenii*, the *oxalic ferment* recently discovered by Kopf. But if the formation of oxalic acid by this and other fungi, and that of acetic acid by the schizophytæ, are regarded as fermentations, why should not the idea be enlarged to cover the formation of tartaric and malic acids, &c., in the higher plants? The author expands this idea, and suggests that the lower plants give by preference molecular fermentations resulting in the production of alcohol, lactic and butyric acids, &c., whilst fermentations of oxidation resulting in carbonic, oxalic, malic, and tartaric acids prevail amongst the higher plants. The migration of calcium oxalate in the tissues, maintained by Schimper, is now admitted by the author, who supports also Schimper's idea that the calcium oxalate is rendered soluble for this migration, whether by free oxalic acid (Wahrlich) or some other substance. He has recognised the presence of calcium oxalate in the expressed and filtered juice of many plants, as many as four crystalline forms of this salt being deposited on allowing these liquids to evaporate. J. M. H. M.

Calcium and Magnesium Oxalates in Plants. By MONTEVERDE (*Ann. Agron.*, **17**, 92—94).—This abstract, from a long memoir in Russian, sums up the principal conclusions arrived at by the author. He shows the presence of these salts in a great number of Gramineæ not hitherto examined. He denies the statement of Schimper that oxalates migrate in the plant tissues, and that of Aé that they disappear gradually in organs etiolated by darkness. The formation of oxalates is greatly promoted by light, both directly and as a consequence of increased assimilation. Blue light is better than darkness, but vastly inferior to orange. The quantity of lime in the soil or nutritive medium has an influence up to a certain point; apparently the normal quantity of oxalic acid formed by the plant combines wholly with lime, if enough is present, and in default with magnesia and other bases. After taking exception to Schimper's classification of the oxalate deposits into primary, secondary, and tertiary, the author remarks that the primary deposits of oxalate are accessory to the transformation of albuminoïds, and not to respiration or to the formation of cellulose. The secondary oxalate appearing in the leaves as the nitrates absorbed by the plant are destroyed is accessory to the synthesis of albuminoïds. J. M. H. M.

Peculiar Odour of Soil. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **112**, 598—599).—With a view to ascertain the cause of the peculiar smell observed when soil is moistened, a quantity of soil, free from all visible vegetable *débris*, &c., was extracted with water at 60°, and the liquid distilled. The distillate has the peculiar odour of the moistened soil, and its intensity increases if the first distillate is redistilled and only the first portion collected. The odour, however, is still perceptible in the residual liquid.

The substance is neither an acid nor an alkali, nor a normal aldehyde; its concentrated aqueous solutions are precipitated by potassium carbonate with production of a resinous ring. When heated with potassium hydroxide, an acrid odour like that of aldehyde resin is developed. It does not reduce ammoniacal silver nitrate, and with alcohol and iodine it gives the iodoform reaction. C. H. B.

Analysis of Fodders, with special reference to the Proteïds. By A. STUTZER (*Landw. Versuchs-Stat.*, **38**, 469—477).—Tables of the analysis of 58 feeding stuffs, showing percentage of non-proteïds, albumin, and indigestible proteïds. E. W. P.

The Climatic Conditions for the Development of Nicotine in Tobacco Plants. By A. MAYER (*Landw. Versuchs-Stat.*, **38**, 453—467).—In a previous communication, the author showed that by the use of a rich and easily assimilable nitrogenous manure, the percentage of nicotine in tobacco plants was increased; in the series of experiments now described, the influence of heat, water, light, and the moisture in the air have been inquired into. Plants grown under glass contained in some cases double the percentage of alkaloïd found in those plants grown in the open and consequently at a lower temperature, and in those plants growing under shelter, a higher temperature corresponded with a higher percentage of nicotine. Full lighting also was accompanied by increase of alkaloïd, even up to 100 per cent. of that contained in plants from which the light was in a measure cut off. A small supply of water seemed to be most beneficial to the full development, an excess being inimical. Increase of the moisture of the atmosphere surrounding the plant, whereby transpiration was diminished, led to an increase in the amount of alkaloïd. E. W. P.

Drainage Waters from Bare and Cultivated Soils. By P. P. Dehérain (*Ann. Agron.*, **17**, 49—82).—The mode of experiment and the first results obtained have been described in a previous memoir (Abstr., 1890, 1459). The results of a second season's observations are given in this memoir. Soils of different natures, obtained from different localities, showed a great difference in retentive power, the ratio of total rainfall (March 1 to November 7) to drainage water being in four cases 3·7, 2·9, 2·9, and 2·3 respectively; the most retentive were the strong clays. The nitrates found in the drainage waters from the same four soils, reckoned into kilos. nitric nitrogen per hectare, were respectively 152·4, 128·1, 62·5, and 45·2; so that the nitrate lost was far from being proportional to the quantity of water percolating; neither had it any connection with the richness in nitrogen of the soils. Ammonium sulphate was added to some pots of bare soil, in order to ascertain whether autumn or spring applications of this salt are preferable, having regard to the nitrogen lost as nitrate in drainage. The results are exhibited in the following table, the sulphate having been added to the soil in November:—

	Drainage water.		Nitric nitrogen.	
	Soil alone.	Soil with ammonium sulphate.	Soil alone.	Soil with ammonium sulphate.
	c.c.	c.c.	mgrm.	mgrm.
Jan. 6 to Jan. 24	2900	1910	52	112
Jan. 24 to Feb. 3	1840	3150	27	178
Feb. 3 to May 4	1960	1950	68	129
May 4 to May 31	3330	2680	124	153
June 3 to July 15......	7850	6820	375	2039
Total.........	17880	16710	646	2611

In this particular season, no considerable nitrification of the ammonium salt occurred until the hot and wet month of July, and the quantity washed through during the winter was certainly less than the roots of the wheat crop could have assimilated.

A previous experiment of the author's having suggested that for some crops (sugar-beet, for example) the presence of humus is as essential to a proper development as a due supply of nitrogen, phosphates, and potash in mineral forms, or at any rate that the latter do not suffice to produce a full development of the crop in the absence of the former, further experiments were undertaken to elucidate this most important point. The mode of pot culture was adopted; several different plants were tried, and the quantity of drainage water in each case, and of nitrate contained therein, were ascertained. The humic matter added to the soil for the purpose of the experiments was obtained by percolation of condensed steam through farmyard manure; such an extract contains, in addition to the nitrogenous organic matter, manurial ingredients in the form of a little phosphate and a considerable quantity of potash. The comparisons were between five pots in each series (1) good soil; (2) exhausted soil; (3) ditto with mineral manures (sodium nitrate, superphosphate, and potassium chloride); (4) the same soil as No. 2, with 1 litre of humic extract; (5) the same soil as No. 2, with 1 litre of humic extract and mineral manures. The plants tried were oats, hemp, peas, rye-grass, and clover; wheat and sugar-beet were included, but failed from accidental causes. The results are, perhaps, comparable amongst themselves, but in no case was as good a crop obtained as would be the case in field culture. The most important results may be thus summarised:—

Oats.—The mineral manures produced full effect; no special influence could be traced to the humus, and the nitrate found in the drainage water was inconsiderable in every case save that of the good soil unmanured, which produced a poor crop.

Hemp.—The worst crops were obtained in the exhausted soil, and in the same with addition of the three saline manures only, and from these two occurred by far the greatest loss of nitrate by drainage, as the following table shows:—

	Pot 1.	Pot 2.	Pot 3.	Pot 4.	Pot 5.
Weight of crop....	35·8	15·5	22·8	25·7	38·4 grms.
N as nitrate in drainage	61	632	1222	40	36 mgrms.

It is true that pot 5 received more total nitrogen, phosphate, and potash than pot 4, but it seems fairly inferable from the poor crop in pot 2, and the loss of nitrate therefrom, that these ingredients, when presented in the purely saline form, could not be fully utilised by this crop.

Rye-grass.—Two cuts were made, and the produce weighed as hay:—

	Pot 1.	Pot 2.	Pot 3.	Pot 4.	Pot 5.
Total produce	66	37	53	51	63 grms.
N as nitrate in drainage water..	33	149	196	140	45 mgrms.

Here also there seems some reason to attribute specific favourable action to the humic matter.

Peas.—In this case the good soil of pot No. 1 (manured year after year) yielded a better crop than any of the rest:—

	Pot 1.	Pot 2.	Pot 3.	Pot 4.	Pot 5.
Total dry produce .	121	66	69	70	83 grms.
N as nitrate in drainage	220	118	132	247	285 mgrms.

Special conditions, and not the mere supply of manurial ingredients, whether as salts or in humus, are necessary to the successful growth of this and probably other leguminous crops; and their indifference, now well established, to the artificial supply of nitrogen is well shown in the large amount of nitrate lost in the drainage water from all the pots.

Clover.—The results are similar to those given by the peas.

	Pot 1.	Pot 2.	Pot 3.	Pot 4.	Pot 5.
Total dry produce .	130	82	85	80	92 grms.
N as nitrate in drainage	269	159	164	196	216 mgrms.

The following interesting table is compiled from the results of these pot experiments :—

Milligrams per Litre of Nitric Nitrogen in the Drainage Water from different Soils under different Crops.

	No. crop.	Oats.	Rye-grass.	Peas.	Clover.	Hemp.
1. Rich soil	38	7·3	1·7	42	31	3·5
2. Exhausted soil	29	0·2	6·0	15	19	22·0
3. No. 2 with chemical manures	—	0·2	10·2	21	21	45·0
4. No. 2 with humic exextract	—	2·3	5·0	40	29	2·0
5. No. 2 with chemical manures and humic extract	—	0·9	2·0	31	32	2·0

Experiments were also made on the best crops for growing during the autumn as green manures, to prevent the great loss of nitrates by drainage which occurs in a wet season after the removal of the summer crop. The autumn of 1890 was, however, very unfavourable for these trials, being very dry, and the long frost which set in about the middle of November, and lasted into January, effectually stopped loss of nitrate, and put an end to the growth of all the autumn green crops.

The following table, nevertheless, is of interest, showing the quantity of nitric nitrogen per hectare lost during the November rains under the different circumstances :—

Summer Crop.	Green manure.	Nitric nitrogen in November drainage.
Sugar beet.................	none	7·5 kilos.
Maize (forage)	none	14·5 ,,
Oats	rape	0·37 ,,
Hemp	none	10·5 ,,
Peas.......................	turnips	0·51 ,,
Rye grass continued in	rye grass	0·38 ,,
Clover ,, ...	clover	1·10 ,,

In dry autumns, it is probable the cost of cultivating and sowing a crop for green manure would exceed the advantage to be gained in preservation of nitrates in the soil; in wet autumns, the green manuring should be very advantageous. The author suggests for this purpose a mixture of rape and vetches, the former to prevent washing out of nitrates, the latter to accumulate nitrogen from the atmosphere. J. M. H. M.

Analytical Chemistry.

Kjeldahl's Process. By V. Edwards (*Chem. News*, **63**, 14—15). —The digestion of the substance, 1 gram for ordinary manure, 0·5 gram for guanos and rich substances, is carried out in the manner already described (*Chem. News*, **59**), except that rather less mercury oxide (about 0·2 gram) will suffice. The distillation of the ammonia is conducted from a 500 c.c. flask resting on a sand-bath and fitted with a rubber stopper, through which passes a tube, which is carried about 3 inches into a small, tubulated retort holding about 110 c.c., and serving to condense the quantity of distillate which will contain all the ammonia. The stopper of the retort is replaced by a cork, through which passes the bent end of a Will and Varrentrap's nitrogen tube containing the standard sulphuric acid. With the modified apparatus, certain precautions are necessary; thus, care must be taken that the heating of the distilling flask is gradually and cautiously performed, and that the gas does not pass too quickly through the Will and Varrentrap tube. G. T. M.

Detection of the Sulphur not combined with Hydrogen in Illuminating Gas. By L. Ilosvay (*Bull. Soc. Chim.* [3], **4**, 714—715).—The gas is passed through a glass tube containing asbestos, which is maintained at a dull-red heat. After being washed by passing through a little water, the gas is filtered through wadding and then traverses a tube containing lead-paper, which is blackened by the hydrogen sulphide formed when the sulphur compounds contained in the gas are heated. W. T.

Estimation of Free and Combined Carbonic Anhydride in Mineral Waters. By H. Bretet (*J. Pharm.* [5], **23**, 339—341). —To 50 c.c. of the mineral water two or three drops of phenolphthaleïn is added, and standard potash solution is run in very slowly towards the end, until the last drop gives a persistent rose tint. The quantity of free carbonic anhydride is double the equivalent of the potash used. Standard potassium carbonate solution can also be employed, and with advantage, as it is more constant than the hydroxide solution; but with the carbonate, one equivalent is the measure of the free carbonic anhydride.

Two or three assays should be made, and the mean result, omitting the first one, should be taken. The amount of solution required by the first assay is added at once in the second assay, and is always too little; more is now added, with gentle stirring, so as to avoid all possible loss of free gas. The total carbonic anhydride is now estimated by adding standard sulphuric acid to the solutions just obtained until a slight excess is present, the solution being boiled to expel the free anhydride, and the excess of acid titrated back with standard potash. J. T.

Estimation of Metallic Zinc in Zinc-dust. By W. MINOR (*Chem. Zeit.*, **14**, 1142—1143).—One gram of zinc is treated with 60 c.c. of potassium dichromate solution (containing 30 grams of the salt per litre, and standardised with pure zinc) diluted with water, and about 20 c.c. of dilute sulphuric acid is run in gradually with constant agitation, so that the operation lasts 20 minutes; more acid is then added, and the excess of dichromate titrated with a solution of ammonium ferrous sulphate containing 150 grams of ferrous sulphate and 75 grams of ammonium sulphate, dissolved in water, and 100 c.c. of strong sulphuric acid, all diluted to 1 litre, and titrated against the dichromate previous to use. The zinc numbers obtained include the cadmium and iron present, which is immaterial when the zinc is only required for purposes of reduction; a method, however, is furnished for calculating the actual proportion of zinc present.

D. A. L.

Estimation of Zinc Carbonate and Silicate in Calamine containing Lead. By W. MINOR (*Chem. Zeit.*, **14**, 1003).—The method previously described (Abstr., 1890, 418) requires modification when lead is present, but the following amended method is applicable to all samples of calamine.

The calamine is boiled for about a quarter of an hour with dilute sodium hydroxide, filtered, the treatment repeated with the residue, which is then filtered off and well washed with hot dilute sodium hydroxide. The lead is separated from the combined filtrates by supersaturating with sulphuric acid, &c.; the solution is then rendered alkaline with ammonia, and the zinc titrated with sodium sulphide; alumina does not interfere with the titration. D. A. L.

Assay of Lead Ores by the Cyanide Process. By A. W WARWICK (*Chem. News*, **63**, 30—32).—The author has carefully determined the value of the cyanide process in the assay of lead ores, using in his investigations (1) a galena with siliceous gangue, the lead, however, containing but a small amount of other base metals; (2) a rather poorer galena containing a considerable quantity of copper pyrites; (3) a pure specimen of galena; and (4) a pure sample of cerussite. He finds that the cyanide assay, when carefully performed, is capable of giving with rich ores results as trustworthy as the best of the other methods, and is to be preferred when the ore is poor. The precautions to be observed are that the temperature is not allowed to rise too high, that the time of fusion does not exceed 20 minutes, and that the amount of cyanide used be not too small. The assay may be conducted in a Battersea crucible. A quantity of cyanide is rammed into it, and on this is placed 100 grains of the ore mixed with about six times its weight of Becker's stick cyanide of potassium, and the whole covered with a layer of cyanide and finally a layer of salt, the total weight of cyanide used being 750 grains. The charge is best heated in a Fletcher's gas furnace at a low red heat for 15 minutes, and at a full red heat for an additional 5 minutes. On breaking the crucible, the button of lead is obtained in a very clean condition.

G. T. M.

Detection of Mercury in Toxicological Researches. By M. T. LECCO (*Ber.*, **24**, 928—929).—It is generally assumed that mercury dissolves easily in hydrochloric acid on addition of potassium chlorate, and that when organic substances containing mercury are treated with hydrochloric acid and potassium chlorate, the whole of the mercury goes into solution. During the examination of a human stomach containing mercury, the author observed that the solution obtained by treatment with hydrochloric acid and potassium chlorate contained scarcely a trace of mercury. The insoluble residue was therefore examined, and found to contain the mercury undissolved. A fresh portion of the stomach was treated with hydrochloric acid and chlorate in a glass dish, and after a short time small globules of mercury were observed on the bottom of the dish which remained undissolved after the organic matter had been destroyed.

The author then treated pure mercury with concentrated and dilute hydrochloric acid and potassium chlorate, both at the ordinary temperature and on the water-bath, and in all cases found that the mercury is difficult to dissolve. Hence it is absolutely necessary to continue the action of hydrochloric acid and chlorate for many hours after the destruction of the organic material when mercury is to be detected.

E. C. R.

Analysis of Sodium Aluminate. By K. J. BAYER (*Chem. Zeit.*, **14**, 736—737).—The author draws attention to the fact that the method of analysis of sodium aluminate proposed by Lunge (this vol., p. 365) has been used by himself for some time (Abstr., 1886, 281, 651). He takes exception to Lunge's remarks as regards the interference of silica, for not only has silica no neutralising effect for the acids, but it is shown that sodium aluminate cannot retain more than traces of silica any more than sodium silicate can contain much alumina, inasmuch as the excess in both cases forms a gelatinous precipitate, which, when washed and air-dried, has the percentage composition SiO_2, 35·24; Al_2O_3, 19·74; Na_2O, 10·55; water at 100°, 25·95; water on ignition, 8·50; corresponding with the formula $Na_2O,Al_2O_3,3SiO_2 + 9H_2O$. This substance forms a very fine, light, probably crystalline powder, readily soluble in acids, sparingly soluble in water, and having an alkaline reaction. When dissolved in a definite quantity of normal acid and titrated back with standard soda and methyl-orange, numbers for both the alumina and the soda present in the compound are obtained; with phenolphthaleïn as indicator, however, the numbers are below those required for the soda present, owing presumedly to the regeneration of the original compound, or the formation of some similar one. The author then shows that the highest possible error attributable to silica is insignificant, and the only defect he recognises in this method of titrating alumina is the indistinctness of the end reaction, which may be overcome to a certain extent by practice or by adding methyl-violet or some such blue colour changed by acids.

It is pointed out that almost all the silica of the raw material in the preparation of sodium aluminate remains behind on lixiviation in the form of $Na_2O,Al_2O_3,3SiO_2 + 9H_2O$, and entails for each per cent. of silica a loss per cent. of 0·57 alumina and 0·34 sodium oxide (compare Abstr., 1889, 213). D. A. L.

Influence of Extractive Matter on the Real Alcoholic Strength of Spirits. By C. Blarez (*Compt. rend.*, **112**, 585—588).—The presence of extractive matter (sugar, glycerol, &c.) in an alcoholic liquid reduces the apparent alcoholic strength by increasing the sp. gr. The results of a large number of analyses of brandy, rum, and tafia have shown that the real alcoholic strength can be calculated from the apparent alcoholic strength by adding to the latter the product of a coefficient into the number of grams of extractive matter per litre. The coefficient $= 0·58 - 0·0108\,d + 0·0000064\,d^2$, where d is the real alcoholic strength. The apparent alcoholic strength and the quantity of extractive matter must be carefully determined. A first approximation is made by proceeding in the manner indicated, substituting the apparent alcoholic strength for the real in the expression for the coefficient. The result is then used in a second approximation, which is generally sufficiently accurate; with 0·4 to 0·5 per cent. of extractive matter only, the first approximation may be taken. C. H. B.

Estimation of Crude Fibre and Starch. By M. Hönig (*Chem. Zeit.*, **14**, 868, 902—903).—When starch is heated steadily at 210° with glycerol, water vapour is at first evolved with frothing, but a clear, transparent, mobile liquid gradually forms, from which, when cool, a mixture of alcohol and ether precipitates the starch quantitatively. Under similar circumstances, cellulose remains unaltered, but glucose caramelises, is partially converted into humous matters, and yields a solution which is not precipitated by the ether and alcohol mixture; whilst albumin, when heated with glycerol, at first coagulates, but subsequently, with the aid of agitation, gradually forms a solution which is neither coagulated when boiled with water nor precipitated by the mixture of alcohol and ether; this solution, however, gives a precipitate with hydrochloric acid, dissolving in excess of the acid, and the usual precipitates with phosphotungstic and phosphomolybdic acids. It hence appears that albumin, like starch, can be made to assume simpler molecular aggregations without undergoing complete chemical change.

The above variations in the behaviour of the substances enumerated, when heated with glycerol, are applied to the estimation of starch and crude fibre in vegetable matter in the following manner:—The finely-pulverised material, along with glycerol, is placed in a test-tube supported in a flask of concentrated sulphuric acid, and gradually heated to 210°; the decomposition is complete in about $\frac{1}{2}$ to $\frac{3}{4}$ of an hour, the tube is then cooled to 130°, the contents poured into 95 per cent. alcohol, the tube rinsed out with water, and ether added.

The precipitate is washed with a mixture of alcohol and ether (5 : 1), drained, and boiled with water; the starch dissolves, and when all the alcohol has been driven off, is inverted and estimated with Fehling's solution: the cellulose, which is always free from nitrogen, is then washed, dried, weighed, ignited, and the weight of the ash deducted. Filtration is facilitated, without any danger of seriously attacking the cellulose, by heating the mixture of starch and cellulose for half an hour with dilute hydrochloric acid. D. A. L.

Analysis of Celluloïds. By H. ZAUNSCHIRM (*Chem Zeit.*, **14**, 905).—The finely-divided celluloïd is well stirred, by means of a platinum wire, with sulphuric acid in the funnel of a nitrometer, and, when dissolved, the nitrogen is estimated in the solution in the usual manner. To prevent interference from camphor, the following treatment is suggested:—Dissolve a weighed quantity of the celluloïd in a mixture of ether and alcohol or in methyl alcohol, mix with a weighed quantity of washed and ignited asbestos or pumice-stone, dry, disintegrate the mass, and extract the camphor with chloroform, dry, and weigh; then extract with absolute methyl alcohol, evaporate, weigh, and examine the nitrocellulose in the nitrometer.

D. A. L.

Gum Arabic and Gum Senegal. By L. LIEBERMANN (*Chem. Zeit.*, **14**, 665—666).—The employment of gum senegal as an adulterant of, or even as a substitute for, gum arabic led the author to investigate the properties of these two gums.

Gum arabic forms rounded or angular, colourless, yellowish, or brownish, and strongly-refractive little lumps; whilst gum senegal is usually in long, straight or curled cylindrical pieces, but occasionally in mulberry-shaped nodules, and is either colourless or faintly-yellow or white, like etched glass, superficially, and lustrous and transparent internally. The two gums are therefore readily detected in the uncrushed condition, but under other circumstances they require further investigation for their identification.

Water dissolves both gums, leaving a residue of wood fibres, these being usually red if from gum arabic and black from gum senegal. Potassium hydroxide and copper sulphate produce a blue precipitate in both solutions; the gum arabic precipitate is more considerable than the senegal precipitate. Moreover, the former is coherent, and rises to the surface; whereas the latter is more flocculent, and remains disseminated in the liquid. The precipitates are only very slightly soluble on warming, and are not reduced even on boiling. Under similar treatment, dextrin also gives a buish precipitate insoluble in the cold, but soluble to a clear, dark-blue solution on warming, which solution is completely reduced by prolonged boiling. By heating with dilute potassium hydroxide for some time, solutions of gum arabic or dextrin become amber-yellow; solutions of gum senegal, on the other hand, scarcely alter or are but very faintly yellow.

Mixtures of the gums arabic and senegal behave, with potassium hydroxide alone, like gum arabic; with potassium hydroxide and copper sulphate, like gum senegal. The blue precipitates from mixtures of dextrin with gum arabic or gum senegal are reduced on boiling, provided the quantity of dextrin is not too small; but when the latter is the case, after thorough warming, the precipitate must first be filtered off, then, on boiling the filtrate, reduction takes place if dextrin is present. When both gums as well as dextrin are present, the precipitate is washed, dissolved in dilute hydrochloric acid, and the gums precipitated by means of a large excess of alcohol; when settled, they are washed and examined by the above methods.

The examination of a sample of gum arabic may be conducted in the following manner:—Dissolve the powdered substance in lukewarm water, examine residue—any gelatinous matter indicating foreign gums; treat the solution with excess of potassium hydroxide and copper sulphate, warm, filter, and examine for dextrin and senegal as described above.

Gum senegal has been stated to be more hygroscopic than gum arabic; but on drying at 105°, the former lost 13·39 per cent., the latter 14·56 per cent., and, on exposure to the moist atmosphere, the former reabsorbed 6·15, the latter 6·34 per cent. of water.

D. A. L.

Formation, Detection, and Significance of Furfuraldehyde. By E. NICKEL (*Chem. Zeit.*, **14**, 836).—The formation of furfuraldehyde being characteristic of certain classes of compounds, such as the carbohydrates and their derivatives (glucosides) and the proteïds, the author gives a simple means of detecting it:—The substance is either submitted to dry distillation in a perfectly clean test-tube, or it is carefully heated with a small excess of concentrated sulphuric acid; in either case, the presence of furfuraldehyde in the vapour is ascertained by its reddening paper charged with an aniline or xylidine salt; or the furfuraldehyde may be identified in solution by the use of well-known reagents, such as α-naphthol, phloroglucinol, &c.

D. A. L.

Sensitive Reaction for Tartaric Acid. By E. MOHLER (*Bull. Soc. Chim.* [3], **4**, 728—729).—Crystals of tartaric acid, when thrown on sulphuric acid of 66° B. containing 1 per cent. of resorcinol and heated gradually, produce a fine, red-violet coloration when the temperature approaches 125°; at 190°, complete carbonisation occurs. The colour is destroyed by the addition of water to the sulphuric acid solution. It has been found impossible to isolate the colouring matter formed, as it is insoluble in ether, amyl alcohol, acetone, chloroform, and benzene.

With other phenols, similar colour reactions are obtained; thus phloroglucinol gives a red, pyrogallol a fine violet, coloration.

These reactions are not given by succinic, malic, citric, or benzoic acids; hence tartaric acid may be readily detected in a mixture with any of these; 0·01 milligram of tartaric acid can be characterised by operating as follows:—

The solution supposed to contain tartaric acid is evaporated to dryness in a small porcelain capsule, 1 c.c. of the resorcinol solution added, and gradually heated to about 125°, reddish streaks first appear, and then the sulphuric acid becomes coloured throughout.

If sugars, gums, or other organic substances which char in contact with sulphuric acid are present, the tartaric acid is precipitated as lead tartrate, the precipitate treated with nitric acid to destroy traces of the organic matter, and the nitric acid driven off; the residue then gives the colour reaction as above.

It is necessary to avoid the presence of nitrates and nitrites, as they give an intense blue coloration with resorcinol, which masks the tartaric acid reaction. W. T.

Estimation of Soluble and Insoluble Fatty Acids in Butter. By W. Johnstone (*Chem. Zeit.*, **14**, 671).—The author claims priority as regards the method of estimating fatty acids in butter described by Bondzynski and Rufi (Abstr., 1890, 838). D. A. L.

New Method of Testing the Purity of Butter. By G. Firtsch (*Chem. Centr.*, 1891, **1**, 283—284; from *Ding. Polyt. J.*, **278**, 422—429).—The method depends on the solubility of the barium salts of the volatile fatty acids of butter-fat. From 0·99—1·01 gram of the clarified fat is heated in a strong flask of 150 c.c. capacity with 50 c.c. of $\frac{1}{10}$ N. barium hydroxide for 6—8 hours at 140° by means of a paraffin-bath. It is frequently advisable to allow the flask to cool at the end of 3 hours in order to bring the little fat, which adheres to the sides of the flask, into the reaction, which is assisted by the frothing up which takes place when the heating is resumed. When the saponification is complete, the contents are passed as rapidly as may be through a filter into a half-litre flask, and washed with boiling water until the flask is full. The separation of the soluble from the insoluble barium salts is perfect excepting in the case

	Per cent. of total combined barium.			
	Ba in insol. salts.		Ba in sol. salts.	
Butters I	68·47	mean 67·26	31·53	mean 32·74
,, II	66·48		33·52	
,, III	65·84		34·16	
,, IV	68·99		31·01	
,, V	67·11		32·89	
,, VI	67·21		32·79	
,, VII	66·75		33·25	
,, VIII	69·80		30·20	
Pig-suet, I	81·04		18·96	
,, II	80·60		19·40	
Tallow	87·07		12·93	
Margarine, I	76·62		23·38	
,, II	75·16		24·84	
Butter, 70 per cent.; suet, 30 per cent.	70·86		29·14	
,, 50 ,, ,, 50 ,,	74·02		25·98	
,, 30 ,, ,, 70 ,,	78·37		21·16	
Cocoa-nut oil	66·98		33·02	
Palm oil	73·24		26·76	

of cocoa-nut oil, which contains lauric acid. The insoluble barium salts are decomposed with 25 c.c. $\frac{1}{2}$ N. hydrochloric acid and warmed on the water-bath, filtered, washed, and weighed.

In the solution of the soluble barium salts, the excess of barium is determined by means of $\frac{1}{10}$ N. hydrochloric acid, as also the total amount of barium as sulphate. From the three determinations, the amounts of the insoluble fatty acids, the soluble fatty acids calculated as butyric acid, and the respective amounts of barium combined with them are obtained. The author's results are given in the table on the preceding page.

By distilling the solution containing the acids from the soluble barium salts, figures were obtained which did not agree with those obtained by the Reichert-Meissl method. The weight of the acids of the insoluble barium salts agreed with those obtained by Hehner's method.

J. W. L.

Analysis of Butter. By M. VIOLETTE (*Chem. Centr.*, 1891, **1**, 286—287, from *Milch-Zeit.*, **19**, 905—906).—After separating the volatile from the non-volatile fatty acids, the author calculates, by means of Duclaux's formula, the ratio of butyric to caproic acid, and the results, as in the table, show that the greater part of the volatile acids consist of butyric and caproic acids.

	Butter [best] (3 samples).	Butter [2nd quality] (5 samples).	Margarin.	Suet.
Butyric acid............	5·33— 6·07	4·62— 5·05	0·47	0·273
Caproic acid............	3·23— 3·66	2 80— 3·06	0·28	0·166
"Concrete" volatile acids	2·80— 3·00	2·40— 3·00	1·33	0·914
Total volatile acids......	8·56— 9·73	7·22— 8·81	0·75	0·439
Solid fatty acids	82·28—82·87	83·83—84·62	93·40	91·120

J. W. L.

Iodine-number for Cocoa-butter. By F. FILSINGER (*Chem. Zeit.*, **14**, 716).—The following are the mean iodine-numbers for cocoas of various origins calculated from the results of numerous determinations:—

Arriba, I	35·1
Arriba, II.	36·8
Carracas, I	34·4
Carupano......................	35·2
Ceylon	35·9
Machala Guajaquil.............	33·4
Puerto Cabello	34·1
Surinam	34·0
St. Thomé	33·5
Trinidad	34·5

Kauka, Bahia, and Porto Plata cocoas have been shown to range between 34·0—37·5; hence it follows the iodine-number for pure cocoa-butter varies between 33·4 and 37·5.

D. A. L.

Fat Analysis. By R. Benedikt (*Chem. Zeit.*, **14**, 835—836).—In course of a very extensive experience and in conjunction with numerous collaborateurs, the author has never obtained an acetyl number in the absence of hydroxy-fatty acids; he therefore unhesitatingly condemns Lewkowitsch's (Proc., 1890, 72—91) results as erroneous, and asserts the correctness of his own.

In a few remarks on the method in question it is pointed out that the alcoholic potash, for the saponification in the estimation of the acetyl number, may be replaced by semi-normal soda in the following manner; the acetylised fatty acid is dissolved in alcohol, titrated with semi-normal soda and phenolphthaleïn, then $1\frac{1}{2}$ or twice as much of the same soda is run in, the whole heated on a water-bath and titrated back with hydrochloric acid. Numbers below the theoretical are obtained for the acetyl acid number of oils containing hydroxy-fatty acids; this has to be taken into consideration when making determinations, and methods of calculation for the purpose are given. The formation of internal anhydrides is suggested as the cause of this depression of the acid number.

As regards the estimation of glycerol, the author recognises he superiority of permanganate over the acetin method, but, nevertheless, regards the latter as of value especially for technical purposes. Attempts to estimate the glycerol by conversion into allyl and isopropyl iodides have not proved successful. D. A. L.

The Elaïdin Reaction with Fatty Oils. By C. Welleman (*Landw. Versuchs-Stat.*, **38**, 447—451).—In testing olive and earth-nut oils by the elaïdin reaction, it was found that the mass solidifies sooner at a lower than at a higher temperature, 13—15 min. at 14°, 2 hours 17 min.—1 hour 7 min. at 18—19°; also if the surface of separation of the strata of oil and mercury and acid be not disturbed at the commencement of the testing, then a longer time is required for solidification. E. W. P.

Resin Oil in Oil of Turpentine. By E. Baudin (*J. Pharm.* [5], **23**, 279—280).—A drop of the suspected oil is placed on a thin slip of unsized paper, and allowed to evaporate spontaneously. After one or two hours, the liquid has disappeared without leaving a sensible stain if pure, but if adulterated with resin oil, a distinct oily stain is left. With 5 per cent. of impurity, no mistake is possible. In doubtful cases, 20 to 30 drops is evaporated to 6 or 8 drops in a porcelain capsule, and this concentrated solution is tested as above. By comparison with known mixtures, an approximate estimation of the amount of impurity present may be made. J. T.

Estimation of Tannin in Hops. By E. Kokosinski (*Chem. Centr.*, 1891, i, 377; *Zeit. ges. Brauwesen, München*, **13**, 571—574).—The method depends on the property of tannin of absorbing iodine in presence of alkaline carbonates.

The solution is prepared by boiling 10 grams of hops, the solution being diluted to 500 c.c. If the hops have been sulphured, a few drops of hydrogen peroxide is added to the water before commencing to boil. The extract is filtered from the hops. The solutions required are: (1) normal solution of sodium carbonate; (2) normal sulphuric acid; (3) $\frac{1}{50}$ N. iodine; (4) $\frac{4}{50}$ N. solution of sodium thiosulphate 9·920 gram in 1 litre; (5) a solution of pure tannin prepared from galls which contains 0·05 gram tannin in 100 c.c.; (6) a freshly prepared solution of starch.

Three flasks of about 100 c.c. capacity, are employed; into the first is put 10 c.c. of water, into the second 10 c.c. of the tannin solution, into the third 10 c.c. of the hop extract. To each flask 4 c.c. of the normal sodium carbonate solution is added, and immediately afterwards 20 c.c. of the standard iodine solution. Flasks 2 and 3 are then tested for free iodine by placing a drop of the solution on to a piece of starch paper, and if free iodine is not present, more of the standard iodine must be added to each flask. The iodine is allowed to react for five minutes, then to each flask 4 c.c. of the normal sulphuric acid is added to neutralise the sodium carbonate, and 10 c.c. of the sodium thiosulphate solution is added to reduce the excess of iodine present. A few drops of starch paste are now added to each flask, and the excess of thiosulphate determined with the iodine solution. The number of c.c. of iodine required to titrate the thiosulphate in flask 1 represents the amount of iodine which has entered into combination with the sodium carbonate, the starch, and other errors which may be inherent to the titration; the amount of iodine used by flask 2 represents that absorbed by the solution of tannin = 0·005 gram plus the amount absorbed in the blank experiment; the iodine used by flask 3 represents that which was absorbed by the tannin of the hops *plus* the amount absorbed in the blank experiment. From these figures, the amount of tannin in the hops may be readily calculated. J. W. L.

Detection of Coniine in a Case of Poisoning. By L. W. ANDREWS (*Amer. Chem. J.*, **13**, 123—128).—A stomach and a jar of soup were submitted to the author for analysis for "strychnine and other poisons." The stomach was immersed in a preservative sold as "bromo-chloralum" (a solution of magnesium and aluminium chlorides with a little bromide), and with this the contents had become mixed, but this did not interfere with the examination. The interior of the stomach was coated with a coffee-coloured scum, and exhibited near the pyloric end some large inflamed patches and numerous small pin-head dots of intense inflammation.

162 grams of the stomach (and contents) were cut up finely, digested for some time with 96 per cent. alcohol and 10 drops of sulphuric acid, filtered, and washed with alcohol. The filtrate and washings were evaporated to one-third at 50°. Light petroleum, benzene, and chloroform, applied successively, failed to extract any alkaloïdal substance from this liquid; it was then made alkaline with sodium hydroxide and filtered, the precipitate being washed with a little alcohol. A portion of this solution and washing (B) was shaken with light petroleum; on subsequent evaporation with a drop of strong hydrochloric acid, the latter turned red and then violet-

blue (a reaction of impure coniine), and a crystalline hydrochloride was left. The following reactions were obtained with this residue:—With phosphomolybdic acid, pale-yellow, amorphous precipitate; with potassio-mercuric iodide, the same; with mercuric iodide, white, amorphous precipitate; with gold chloride, pale-yellow, microcrystalline precipitate; with strong sulphuric acid and potassium dichromate, no colour except from gradual reduction of chromic acid; with picric acid, no change; with platinum tetrachloride, no change; with potassium dichromate, no precipitate; with iodine in potassium iodide solution, brown precipitate, which disappeared and was reproduced on further addition of the reagent.

The rest of the solution B was shaken, a part of it with choloroform and part with ether. The hydrochloride from the former solvent was hypodermically administered to a cat; great dilation of the pupils, a blue nose, violent trembling, laboured and irregular respiration, and partial paralysis of the hind-legs were the symptoms that ensued; after a nearly complete torpor had set in, recovery followed in four hours. From the ether solution, microscopic, oily globules smelling of coniine were obtained.

By working up a further portion of the stomach especially for the purpose, sufficient of the hydrochloride was obtained for a quantitative determination of the hydrochloric acid, which was found to agree with that calculated for the known formula of coniine hydrochloride.

The usual plea that the alkaloïd detected was an unnamed ptomaïne was set up by the defence. A. G. B.

Addition of Phenolphthaleïn to Margarin. By E. Holm (*Bied. Centr.*, 1891, 138—139).—Small quantities of phenolphthaleïn added to milk, which was afterwards churned, were readily detected, and appeared to be evenly distributed throughout the mass of butter produced, and could be recognised even after the butter had been kept for three months. Phenolphthaleïn introduced into margarin was also easy of detection, although the colour reaction was somewhat feebler than with butter. The quantity capable of detection in this case was one of phenolphthaleïn in 50,000 parts of margarin.

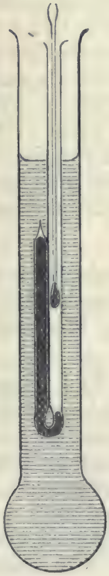
E. W. P.

A New Test for Proteïds. By J. A. MacWilliam (*Brit. Med. J.*, **1**, 1891, 837—840).—Salicylsulphonic acid is recommended as a powerful precipitant for proteïds. It precipitates all varieties of these substances; and solutions containing only 1 part of proteïd in 100,000 of water still show an opalescence when treated with a few drops of the reagent. The precipitate produced with albumins and globulins is not soluble on heating; that produced with albumoses and peptones is dissolved, reappearing when the liquid cools. The test is further recommended as a means of detecting minute quantities of proteïd in urine. No normal or other abnormal constituent of the urine is precipitated by the reagent. W. D. H.

General and Physical Chemistry.

Boiling Point Determination with Small Amounts of Material. By A. Schleiermacher (*Ber.*, **24**, 944—949).—The boiling point of a substance, the amount of which is so small that the ordinary method of distillation cannot be applied, can be determined by measuring the temperature at which the pressure of the saturated vapour of the substance in question is equal to that of the atmosphere. The method described in this paper is based on the above principle.

A glass tube is taken, about 50 cm. long and 6—8 mm. in diameter, and is drawn out at one end to a thickness of 1—2 mm. in diameter. This end is then again drawn out to a fine capillary of about 50 mm. in length, and cut off so as to leave a small portion of the wider tube at the end of the capillary. The tube is then bent into U-form, the open limb being left about twice as long as the closed limb. For this purpose the tube is heated until it contracts to about half its original diameter, and is then bent so that the two limbs are parallel, and nearly touching each other. The substance experimented with is introduced into the open limb, and by inclining the tube, transferred to the closed limb, mercury being then added in like manner. The substance, which is now in the closed end of the tube, is gently warmed, until it commences to boil, the vapour driving any air which may remain in the tube out at the capillary.



The capillary is then sealed. At the end of this operation, the tube should contain nothing but the substance experimented with and mercury. Any mercury remaining in the open end of the tube is now removed, and the tube is placed in a bath for the purpose of heating, the whole arrangement being that shown in the drawing. The thermometer is placed in the open tube, and its temperature will indicate that of the heated substance.

On heating, the substance will, after a time, commence to volatilise, and the mercury will rise in the open tube. When the mercury, in both tubes, stands at the same level, the vapour pressure of the substance is equal to that of the atmosphere, and the temperature, therefore, will be that of the boiling point of the substance under the barometric pressure at the time of the experiment. This may be corrected in the ordinary manner, and the normal boiling point thus obtained; or by roughly graduating the tube the apparatus itself may be employed for obtaining directly the boiling point under normal atmospheric pressure. Thus, if the barometric pressure were 750 mm., the mercury would be allowed to rise in the open tube until its level was 10 mm. higher than that in the closed tube. The thermometer would now indicate the normal boiling point. Another advantage of this apparatus is that the correction for that portion of the thermometer which ordinarily escapes heating becomes unnecessary. For the apparatus can obviously be taken of such a size that both bulb and thread of the thermometer shall be below the level of the liquid in the bath, and, therefore, both be uniformly heated.

In carrying out an experiment it is advisable to take several readings, both when the tube is being heated and when it cools. The mean of these determinations gives the boiling point with great accuracy. This is illustrated by experiments performed with substances of known boiling point. The vapour pressure of the mercury itself does not appear to influence the results, even at as high a temperature as 300°. The minimum quantity of substance that can be taken for a determination is given by the condition that the vapour must be saturated, so that a trace of liquid must always remain in the vessel on vaporisation. If v is the volume occupied by the vapour, d its density, and l the specific gravity of air at the boiling temperature (about 0·0012), the minimum quantity of substance necessary is given by vdl. H. C.

Note.—The author appears to have completely overlooked the fact that H. Chapman Jones (Trans., 1878, 175) has described in full detail an apparatus practically identical with the above.

Theory of Dissociation. By J. Traube (*Ber.*, **24**, 1321—1327; compare this vol., pp. 390 and 638).—The author compares the determinations of the freezing point of aqueous sugar solutions made by Raoult and Arrhenius, those of the former being preferred on account of the more numerous precautions observed. An account is also given of the manner in which the author's own determinations were conducted; the results obtained agree closely with those of Raoult, and confirm the statement that "the osmotic coefficient of all organic substances, in sufficiently dilute solutions, is identical, or almost so, with that of many salts;" the only difference is one of degree, or, in other words, the dissociation of the molecular aggregates of organic compounds in solution usually commences at concentrations where that of salts is completed. Pickering and Raoult, in private communications to the author, express similar views.

Upholders of the theory of electrolytic dissociation have, therefore, to consider whether it can be extended so as to include solutions of all organic substances, and, if so, into what ions these are resolved.

J. B. T.

Precipitation. By G. WATSON (*Chem. News*, **63**, 109—111).—In a previous communication (Abstr., 1890, 847), the author expressed an opinion that the transition of certain precipitates from the amorphous to the crystalline form was due to the combined influence of the surface energy of abraded glass and condensation of the precipitated material. A series of new experiments with antimony chloride, sodium antimonate, calcium hydrogen orthophosphate, and calcium carbonate, have led to the conclusion that the change in question is due to the lower solubility of the crystalline form as compared with the amorphous form, and, in fact, the latter can be avoided by using sufficiently dilute solutions. As it is, the amorphous form is first precipitated, then dissolves in the circumambient solution, until the latter is supersaturated; crystallisation then sets in, liberating mother liquor, ready to dissolve more of the amorphous precipitate; the solution, supersaturation or saturation, and crystallisation continue until all the amorphous salt is converted into crystals.

Similar cycles of phenomena have been pointed out by C. Winkler (Abstr., 1885, 871) in the case of arsenious oxide, and by H. Le Chatelier (Abstr., 1883, 712; 1885, 304; 1888, 1030) in connection with gypsum, sodium sulphate, and calcium silicates and aluminates.

The author has attempted, unsuccessfully, to obtain arragonite crystals from amorphous calcium carbonate at ordinary temperatures (below 30°) by introducing these crystals into the liquid.

A practical bearing, in the case of the antimony salt, is pointed out, inasmuch as fresh antimony does not pass into solution until that already in solution has been removed; it is suggested that cotton impregnated with tannin would serve to remove the antimony from solution, and so set the cycle of changes at work; the amorphous antimoniacal precipitate in this way would serve, in dyeing operations, as a substitute for the more expensive tartar emetic.

D. A. L.

Automatic Sprengel Pump. By H. L. WELLS (*Ber.*, **24**, 1037—1041).—In the Sprengel pump described in this paper, the mercury is raised automatically by means of water pressure. Water enters at A (Fig. 1) into the small bottle, from which it flows out again through the tube B. M contains mercury, which can flow into the bottle through the tube ending in the valve V. This valve allows the passage of liquid from the inside, but is closed by outside pressure. Its construction is shown in Fig. 2. The glass tube is filed down until a small opening, *b*, has been made, and over this a small piece of indiarubber tubing is placed, with an incision, *a*, on the opposite side to the opening *b*. When mercury flows into the bottle, it is forced by the water pressure into the tube B. In this it will rise until the level is very nearly that of the mercury in M, when its pressure will close the valve. The water pressure will then force the mercury up the tube B, and out at the top, when, the pressure being released, the valve will again open, and the above operations will be repeated.

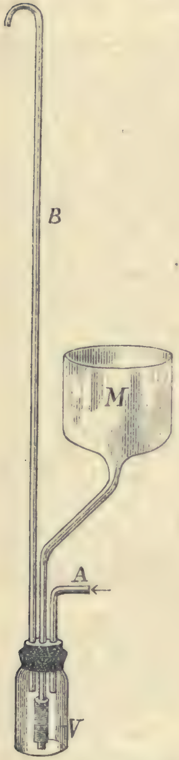


FIG. 1.

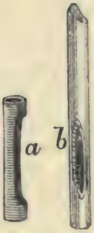


FIG. 2.

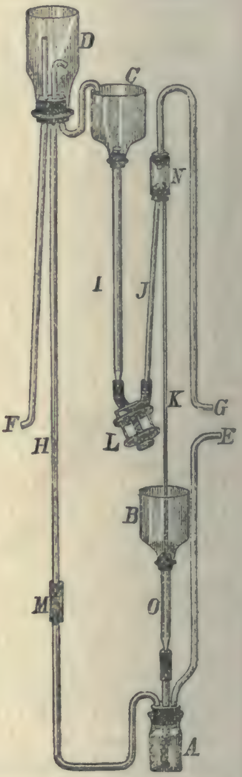


FIG. 3.

In Fig. 3, this method of raising mercury is shown, attached to the Sprengel pump. Water enters at E, carries the mercury up the tube H, and flows out at F, whilst the mercury passes through the side tube into the reservoir C of the Sprengel pump. The downward bend in the tube H lengthens the column of mercury which is periodically carried up this tube. The distance from B to A determines the total length of the mercury column, but this distance will itself depend on the water pressure at command. Usually a distance of 500—600 mm. will be found sufficient, and the tube K of the

Sprengel pump being about 1500 mm. long, the whole apparatus will have a height of about 2 metres. H. C.

Atomic Weights. By F. W. Clarke (*Chem. News*, **63**, 76—77). —A table of atomic weights, O = 16, H = 1·007, computed by the author from the most recent and trustworthy sources, and issued by the Committee of Revision and Publication of the U.S. Pharmacopœia.

D. A. L.

Inorganic Chemistry.

Silent Discharge and Chlorine. By H. M. Vernon (*Chem. News*, **63**, 67).—When subjected to the influence of the silent electrical discharge, chlorine, either alone or saturated with bromine, showed no tendency to condensation. The author regards this insensibility as a function of univalency, and states reasons for supposing that of all the elements probably oxygen is the only one capable of undergoing such condensation. D. A. L.

Magnus' "Black Sulphur." By F. Knapp (*J. pr. Chem.* [2], **43**, 305—320; compare Abstr., 1887, 110; 1888, 1163).—Magnus' "black sulphur" is best obtained by suddenly heating a mixture of sulphur and oil, certain precautions being taken in order to obtain the maximum yield. The author dissolves almond oil (5—10 drops = 0·2—0·4 gram) in ether, mixes the solution with flowers of sulphur (50 grams) in a mortar, and evaporates the ether. A portion of the mixture thus prepared is dropped from the point of a knife on to the bottom of a red-hot platinum crucible; almost immediately the bulk of the mixture disappears, and a loose, black residue is left; the crucible is at once cooled on an iron plate, and the residue emptied into another vessel. The crucible is again heated to redness, and another portion introduced, the process being thus repeated until the whole mixture has been heated; it is best to keep one hand on the gas-cock to alternately raise and lower the flame, as the decomposition takes place more rapidly on the sides than on the bottom of the crucible. Neglect of the points here mentioned greatly diminishes the yield, which in any case is very variable and small; as a mean of 23 experiments, the author obtained 0·685 gram of "black sulphur" from 100 grams of sulphur and 10 drops of oil. 10 drops of oil similarly treated by itself gave only 0·011 gram of residue, or 1·60 per cent. of the "black sulphur."

"Black sulphur" generally contains a little yellow sulphur and, unless pure materials have been used, a considerable quantity of ash, amounting in one case to 9·7 per cent.; it is very slightly hygroscopic. The difficulty of regulating the temperature of the platinum crucible makes it difficult to obtain a homogeneous product, so that its density varies between 2·622 and 1·843, even when prepared from ash-free substances and previously heated to expel yellow sulphur. It is insoluble in hot and cold water, alcohol, ether, hydrochloric acid, nitric acid, aqua regia, ammonia, caustic alkalis even when concentrated, and potassium cyanide. When evaporated with an alkaline hydroxide solution, it is attacked just as the hydroxide is becoming solid, and dissolves to a humus-brown mass, soluble in water with a deep-brown colour; acids precipitate a brown substance from the solution. When heated in air, it first loses moisture and yellow sulphur, but undergoes no other change until a temperature of 200—300° is reached, when sulphurous anhydride is formed; at a red heat the residue takes fire. When heated in the absence of air, no sulphurous anhydride is evolved, but the "black sulphur" slowly loses weight, and does not cease to do so until it has been exposed for many hours to a red heat; the empty space in the tube remains clear and colourless throughout the heating, no empyreumatic vapours or brown vapour of sulphur being evolved; the residue obtained when the weight is constant burns entirely away in the air, and is not influenced in quantity if the heating is conducted in carbonic anhydride; the mean of all experiments gave 43·59 per cent. as the amount of this residue. If the delivery tube of the vessel in which the "black sulphur" is heated dips under potash, much potassium sulphide is formed, although no ordinary brown vapour of sulphur is seen.

The sulphur was estimated in the "black sulphur," previously gently heated to expel moisture and yellow sulphur, by evaporating a portion with potassium hydroxide and potassium nitrate solutions, and heating the residue until it was white; three determinations gave 53·77, 56·76, and 57·07 per cent. of sulphur respectively. The residue left at a red heat contained 22·78 per cent. of sulphur as a mean of three determinations. Thus 44—46 per cent. of the total sulphur is expelled at a red heat, whilst the residue contains some 10 per cent. of sulphur and 33—34 per cent. of carbonaceous matter. Potassium dichromate and bromine dissolve only some 13—14 per cent. of the total sulphur.

Magnus' "black sulphur" is evidently not in itself a modification of sulphur, but consists of such adhering to, or condensed with, a carbonisation product of the oil, itself containing sulphur. This carbonisation product is essential to the production of the modification as affording a surface for condensation or adhesion. The new form of sulphur does not vaporise below a temperature far above the boiling point of yellow sulphur; its vapour is colourless instead of brown; it gives off sulphurous anhydride below a visible heat without combustion.

If it be granted that "black sulphur" contains a modification of sulphur, many other phenomena are brought to mind as probably due to such, especially as the chief manifestation of the modification in question is the production of a blue colour. When "black sulphur" is rubbed with levigated kaolin, a light-blue colour is developed; when it is evaporated with potassium hydroxide and potassium nitrate solutions, a blue ring is formed in the dish; the same is the case when the solution of the sulphur vapour in potassium hydroxide (see above) is evaporated.

The new modification of sulphur is evidently unstable in the free state, but can readily exist in contact with any surface which affords a substratum for its development. As examples, the author quotes the blue colour developed by sulphur on platinum, silver, and lead sulphide; the blue colour of ultramarine, which is so readily destroyed by acids because the substratum of silicates is disturbed, and the sulphur changed into the yellow modification; the momentary blue colour produced when hydrogen sulphide is added to ferric chloride, only wanting permanency, because there is no surface for adhesion; the solution of sulphur in sulphuric anhydride, and other phenomena. The blue-coloured modification of sulphur *en masse* would appear to be a dull black, in which form it may exist in Spence metal, made by fusing sulphur with ferrous sulphide, and may play a part in the vulcanising of rubber. In conclusion, the author expresses the opinion that Schützenberger's compound Pt_2S_2C, obtained by the action of carbon bisulphide vapour on platinum sponge at a dark-red heat (this vol., p. 19), is nothing more than a manifestation of this sulphur. A. G. B.

Thiosulphates. By A. Fock and K. Klüss (*Ber.*, **24**, 1351—1355). —*Potassium Mercuric Thiosulphates.*—The salt $5K_2S_2O_3,3HgS_2O_3$, which has already been prepared by Rammelsberg (*Ann. Phys. Chem.*, **56**, 315) and by Herschel (*Gmelin-Kraut*, Bd. 3, 852), is obtained when freshly precipitated mercuric oxide is dissolved in a solution of potassium thiosulphate and the alkaline liquid evaporated on the water-bath; it separates from an aqueous solution in colourless crystals belonging to the monosymmetric system; $a : b : c = 0·332 : 1 : 0·318$, $\beta = 88° 9'$; these do not blacken on exposure to light. The compound $3K_2S_2O_3,HgS_2O_3 + 3H_2O$ is prepared by adding an excess of potassium thiosulphate to a solution of the last-mentioned salt, and evaporating over concentrated sulphuric acid; it forms small, colourless crystals also belonging to the monosymmetric system; $a:b:c = 1·4843:1:0·9463$, $\beta = 78° 55'$; these are stable in the air and towards light, but become opaque on treatment with water. When potassium thiosulphate is added in very large excess, and the solution evaporated at about 35°, small, prismatic crystals, having the composition $5K_2S_2O_3,HgS_2O_3 + H_2O$, separate; they belong to the asymmetric system; $a : b : c = 0·7034 : 1 : 0·6761$; $A = 88° 42'$, $B = 93° 39'$, $C = 88° 32'$; $\alpha = 88° 36'$, $\beta = 93° 41'$, $\gamma = 88° 27'$; they were not sufficiently perfect for a complete optical investigation.

The salt $K_2S_2O_3,Hg(CN)_2 + H_2O$, which, according to Kessler (*Ann. Phys. Chem.*, **74**, 274), exists also in an anhydrous modification, is prepared by dissolving equal weights of potassium thiosulphate and mercuric cyanide in water, and adding alcohol, or evaporating the solution over concentrated sulphuric acid, when it separates in large, colourless prisms which become yellowish to brown in the air, and develop the odour of hydrogen cyanide; they belong to the quadratic system; $a : c = 1 : 0·54635$, but were too opaque for complete optical investigation. A. R. L.

The Soluble Phosphoric Acid Compounds of Superphosphates. By J. Stoklasa (*Landw. Versuchs-Stat.*, **38**, 401—410; compare *ibid.*, 197—225, and Abstr., 1890, 695).—*Action of Dicalcium on Monocalcium Phosphate.*—Dicalcium phosphate, $CaHPO_4 + 2H_2O$, is prepared from the decomposed monocalcium salt by precipitating the solution of sodium phosphate and acetic acid with calcium chloride. The washed precipitate is slowly dried over sulphuric acid. It forms microscopic, rhombic plates. When dicalcium phosphate (5·49 grams) and orthophosphoric acid (3·86 grams) in 2 litres of water are kept for 48 hours, the free acid disappears and the monocalcium salt is formed. A solution of pure monocalcium phosphate (1 : 200) dissolves 0·025 to 0·03 gram of dicalcium phosphate; if the monocalcium salt contains free acid, this reacts with the dicalcium salt with formation of monocalcium phosphate until the solution is saturated. In presence of much monoferric phosphate, free phosphoric acid acts on dicalcium phosphate, monocalcium phosphate being produced. The so-called soluble phosphoric acid contained in solutions of superphosphates is derived from the soluble dicalcium salt as well as from the monocalcium salt. Dicalcium phosphate is a chief product of the decomposition of monocalcium phosphate in superphosphates and in the soil. Monocalcium phosphate is not decomposed by dicalcium phosphate.

Action of Tricalcium Phosphate.—Tricalcium phosphate, $Ca_3(PO_4)_2 + 2H_2O$, decomposes monocalcium phosphate with formation of dicalcium phosphate. The action is very slow; after 240 days, 0·59 gram of phosphoric acid as monocalcium salt was found. The action is quicker when the finely-powdered and well-mixed salts are heated at 100°; after six hours, 54·3 per cent. of soluble phosphoric acid was found.

Free phosphoric acid and tricalcium phosphate (eq. mol. wt.) have no action on monocalcium phosphate; dicalcium phosphate is formed. If an excess of tricalcium phosphate is present, this will react with the monocalcium salt as described above. The amount of free acid present is of great importance.

When superphosphate contains 15·4 per cent. of soluble phosphoric acid, of which 8·2 per cent. is free acid, there may be 4 per cent. of phosphoric anhydride as $Ca_3(PO_4)_2$; the amount of monocalcium salt will increase until at last all the phosphoric acid of the tricalcium phosphate has become soluble.

When dilute sulphuric acid, or only a slight excess of sulphuric acid, is used, free phosphoric acid is formed; when stronger acid, or when an excess of acid, is used, a small amount of phosphoric acid is produced, and reactions can take place with formation of dicalcium phosphate. Calcium sulphate plays an important part in these processes; it frequently causes the monocalcium phosphate to become coated with the tricalcium salt and hinders the action of free phosphoric acid. These processes are influenced by the degree of concentration of the sulphuric acid, by the amount of acid used, by the degree of fineness of the material (when coarsely-ground, more tricalcium phosphate is formed), by the amount of chalk, calcium fluoride or chloride present, by the length of time the heaps are left, and by the degree of temperature. N. H. M.

Beryllium. By G. Krüss and H. Moraht (*Annalen*, **262**, 38—61).—This paper gives a detailed description of the methods employed in the preparation of pure beryllium sulphate (compare Abstr., 1890, 697), and in the determination of the atomic weight of beryllium by the conversion of the sulphate into the oxide. The value which the authors consider to be the most correct is Be = 9·027, O = 15·96 (compare Abstr., 1890, 1375). F. S. K.

Behaviour of Preparations of Zinc Sulphide. By J. Cawley (*Chem. News*, **63**, 88—89).—Zinc sulphate or chloride, previously freed from iron, manganese, lead, tin, &c., is precipitated by an alkaline or alkaline earthy sulphide, the precipitate is dried, ignited at a red heat, thrown while hot into water, levigated, washed, dried, and finely pulverised. The pigment prepared in this manner is excellent for whiteness, body, and covering power, and is comparatively innocuous; it is, moreover, not discoloured by hydrogen sulphide; it has, however, the disadvantage of blackening in sunlight, but recovers its original whiteness in a more permanent condition when placed in the dark. The darkening does not take place in the perfectly dry pigment hermetically sealed in a glass tube, nor when pure material is exposed to sunlight; if, however, the pure material is calcined even slightly, it becomes sensitive. The darkening is accelerated by moisture, and augmented by damping the zinc-white with zinc sulphate solution. Attempts were made to remove any sulphate from the zinc-white by treatment with potassium, sodium, barium, calcium, or magnesium hydroxide; about 0·5 per cent. of freshly precipitated magnesium hydroxide proved the most effective, but increased the tendency of the zinc-white to frit when ignited, and consequently impaired its value as a pigment, this difficulty being overcome by the use of salt. The author ultimately succeeded in preparing a pigment which as a rule does not darken, in the following manner:—Boiling hot, concentrated solutions of the zinc salt and barium sulphide are used; the precipitate is mixed with 0·5 per cent. of fresh magnesium hydroxide and with pulverised sodium chloride, filtered, dried, coarsely crushed, and mixed with 3 per cent. of ammonium chloride before ignition. The reason for the immunity of this preparation is open to investigation, which the author invites; it was at first suggested that the blackening was due to liberation of metallic zinc in accordance with the reactions $ZnS + 2ZnO = 3Zn + SO_2$ and $ZnS + ZnSO_4 = Zn_2 + 2SO_2$; but this explanation is, in the face of the more recently observed facts, untenable. D. A. L.

Atomic Weight of Lanthanum. By B. Brauner (*Ber.*, **24**, 1328—1331).—Lanthanum is probably a trivalent metal with an atomic weight of 138·21 (O = 16); this number was found by the author, and is identical with the results of Cleeve and of Bettendorff. Winkler (this vol., p. 802) describes the metal as quadrivalent with the atomic weight 180; the lower equivalent of 45 was obtained by Rammelsberg, Zschiesche, and Erk, but their material was almost certainly contaminated with yttrium compounds, which would fully account for the difference. With an atomic weight of 180, the atomic heat of lanthanum is 8·07, which makes it unique in its variation from the law of Dulong and Petit. From its position between cerium and thorium, and ytterbium and tantalum, the molecular volume of the oxide should not exceed 26; with the higher atomic weight, the molecular volume is 33; with the lower, 25·0. Lanthanum is the most positive metal of the rare earths; an element occurring between those above mentioned, and forming an oxide RO_2, should only exhibit feebly basic properties.

The hydrogen compound of lanthanum described by Winkler (*loc. cit.*) is probably a mixture of 3 mols. LaH_2 and 1 atom of lanthanum, or it may be a compound, La_2H_3, the composition of which agrees almost exactly with Winkler's analysis. In this case the type of the hydrogen compounds of lanthanum and cerium is a periodic function of the atomic weight. J. B. T.

Atomic Weight of Chromium. By C. MEINEKE (*Annalen*, **261**, 339—371).—The author has made a careful determination of the atomic weight of chromium by estimating (1) the quantity of silver and of chromium in silver chromate and in silver chromate ammonia, $Ag_2CrO_4,4NH_3$; (2) the quantity of oxygen in these two compounds; (3) the quantity of oxygen in potassium dichromate; and (4) the quantity of oxygen and of chromium in ammonium dichromate.

The silver chromate ammonia was prepared by treating an aqueous solution of pure silver nitrate with a solution of pure potassium chromate, and crystallising the precipitate twice from hot ammonia; the silver chromate was obtained by evaporating an aqueous solution of the ammonia compound.

The potassium dichromate was prepared from pure potash and pure chromic acid; it was free from sulphuric acid, alkaline earths, and metals of the iron group. The ammonium dichromate was obtained by repeatedly recrystallising the purest commercial salt; it contained 0·2 per cent. of potash.

In estimating the silver and the chromium in the silver salts, a weighed quantity was placed in a porcelain crucible, covered with dilute alcohol, and digested with hydrochloric acid, first at the ordinary temperature, and then at 60—70°. The precipitated silver chloride was washed by decantation until free from chromium, dried, and weighed in the original crucible. The filtrate and washings from the silver chloride contain, besides chromium chloride, a considerable quantity of silver chloride, which is kept in solution by the chromium chloride; the silver was precipitated from this solution with hydrogen sulphide and weighed as sulphate.

The oxygen determinations were made by a modification of the method described by Zulkowski (*J. pr. Chem.*, **103**, 351) as follows:—The salt (about 0·5 gram) was dissolved in dilute ammonia, the silver precipitated with potassium iodide, the solution warmed and filtered, and the precipitate washed with water; the filtrate and washings were mixed with solid potassium iodide (5 to 6 grams), then with a solution of pure phosphoric acid (containing about 2½ grams of phosphoric anhydride) and dilute (1 : 1) sulphuric acid (1 c.c.), and titrated with sodium thiosulphate. A special form of burette for use in very accurate analysis is described; the titration was carried out in phosphoric acid instead of in sulphuric acid solution, as the end reaction is then more sharply defined. Instead of using iodine for standardising the thiosulphate solution, the author found it advantageous to employ potassium diiodate in the iodometric analyses of the dichromates, as it is more convenient to weigh, and its solutions are less liable to undergo change. This salt was prepared by evaporating a solution of commercial potassium iodate with a slight excess of iodic anhydride, the product being purified by recrystallisation; it is soluble in 18·63 parts of water at 17°, and its sp. gr. is 3·955. On adding potassium iodide to a neutral solution of the diiodate, the following reaction takes place:—$6KHI_2O_6 + 5KI = 11KIO_3 + 6I + 3H_2O$, 1 atom of iodine being liberated from 1 mol. of the diiodate. In presence of an acid, the reaction is expressed by the equation $KHI_2O_6 + 10KI + 11HCl = 11KCl + 6H_2O + 12I$. Taking the atomic weights of oxygen, chlorine, and silver as 15·96, 35·37, and 107·66 respectively, the atomic weight of chromium, calculated from the proportion $4AgCl : Cr_2O_3$, was found to be 51·99 (maximum, 52·12; minimum, 51·92) as the average of nine experiments. From the average of four estimations of the oxygen in silver chromate, the atomic weight was found to be 52·00, the result of the complete analysis of this salt being on the average $Ag_2O = 69·856$ per cent., $Cr_2O_3 = 22·930$ per cent., and $O = 7·228$ per cent. (total 100·14 per cent.). The iodometric estimations in the case of silver chromate ammonia gave $O = 6·007$ per cent. as the average of six experiments, from which the atomic weight of chromium is found to be 52·04.

The average of 12 determinations of the oxygen in potassium dichromate gave $Cr = 51·91$, and nine experiments with ammonium dichromate, $Cr = 51·94$; five gravimetric determinations of the chromium in ammonium dichromate gave as the average result $Cr = 51·99$.

The extreme values, calculated from 36 experiments, are 52·12 and 51·83; excluding those values which are above 52 or below 51·9, there remain 28 lying between these limits. The iodometric determinations, which are probably very accurate, give as the average result of 21 analyses $Cr = 51·94$, four experiments, which gave values below 51·9, not being taken into account. All the weights from which the above results are calculated are reduced to 0° and a vacuum.

The author concludes with a criticism of the methods employed by other chemists for determining the atomic weight of chromium; he considers Rawson's result ($Cr = 52·01$, Trans., 1889, 213), is highly trustworthy, but points out that when the weights are reduced to 0° and a vacuum the above value becomes 51·98. F. S. K.

Molybdovanadates. By C. Friedheim (*Ber.*, **24**, 1173—1184; compare Abstr., 1890, 1066).—The analogous behaviour of the compounds of tungsten and molybdenum make it probable that the molybdovanadates can be considered as double salts like the tungstovanadates. The author discusses the work of Gibbs (Abstr., 1884, 161, 560, 713) and Milch (*Dissertation*, Berlin, 1887), who have described a list of salts of so-called complex acids obtained by the action of molybdic acid on normal ammonium vanadate, or of vanadic acid on acid ammonium molybdate. He shows that the salts of these complex acids can also be considered as double salts. Thus, Milch, by the action of molybdic acid on normal ammonium vanadate, obtained the compound $3(NH_4)_2O,2V_2O_5,4MO_3 + 11H_2O$. The author also obtained a compound of the same composition, together with ammonium divanadate. He considers that the first stage of the reaction is the production of $2(NH_4)_2O,2V_2O_5$ and $2(NH_4)_2O,2MO_3$. These two compounds then act on one another, 1 mol. of the former combining with 2 mols. of the latter to form the double salt or isomorphous mixture $(NH_4)_2O,2V_2O_5 + 2[(NH_4)_2O,2MO_3] + 11H_2O$, which is the so-called complex salt described by Milch. Experiments under varying conditions are described, and equations are given expressing the products of the reactions as double salts. The free acid of these salts could not be obtained.

The author finally discusses the constitution of salts of complex acids and double salts in general. E. C. R.

Vanadium Fluorides. By E. Petersen (*Ber.*, **24**, 1307).—A note regarding the priority of the discovery of three vanadium fluorides, which were first described by Piccini and Giorgio in 1888, and, shortly afterwards, independently by the author. J. B. T.

Atomic Weight of Osmium. By K. Seubert (*Annalen*, **261**, 257—272).—In a series of experiments carried out some time ago, the atomic weight of osmium was found to be 191 as the average of several not very closely-agreeing determinations (compare Abstr., 1888, 921); the author has undertaken a fresh investigation of the subject with a different sample of the metal and with improved apparatus, but employing the same method as before, namely the analysis of potassium osmiochloride, K_2OsCl_6. Ammonium osmiochloride, $(NH_4)_2Os_2Cl_6$, was also analysed.

Three samples of the potassium salt were used: one was prepared directly in the manner described below, another was obtained from the sodium salt, and the third was a portion of the salt remaining from the previous experiments. The ammonium osmiochloride was prepared from the sodium salt.

In preparing potassium osmiochloride and the corresponding sodium salt, it was found advantageous to heat the mixture of finely-divided metal and alkaline chloride in a stream of hydrogen immediately before passing the chlorine; when this precaution is adopted, only a very small quantity of osmium chloride sublimes on to the cooler portions of the tube; whereas, when it is neglected, volatile products, such as perosmic acid, are formed in much larger quantities, owing to the metal having undergone oxidation by exposure to the air.

Fusion with sodium chloride in a stream of chlorine proved to be the easiest method of preparing a pure double salt; the chlorine is so rapidly absorbed that, unless care is taken to provide a rapid stream of the gas, air is drawn into the apparatus. After keeping the mixture at a dull-red heat for some time, it is allowed to cool, and the dark carmine-red mass dissolved in pure water; the concentrated solutions of the osmiochloride do not change very quickly, but dilute solutions soon become greenish, a black powder being deposited, and an odour of perosmic acid observed; solutions of potassium and ammonium osmiochloride show a like behaviour. It is necessary, therefore, to employ for analysis only those crystals which are deposited from the hot, saturated solution in the course of 12 hours, and to use only small quantities of ice-cold water in washing the salt.

In preparing the potassium and ammonium salts from the sodium salt, a concentrated solution of the latter is mixed with 50 per cent. alcohol (1 vol.) and a solution of pure potassium chloride or ammonium chloride in 50 per cent. alcohol added in slight excess; the potassium or ammonium salt, as the case may be, is precipitated, almost immediately, as a dark-red, crystalline powder, and is first washed with dilute alcohol, and then recrystallised from hot water. The salts were dried over phosphoric anhydride under reduced pressure at the ordinary temperature; in this way they are not obtained perfectly anhydrous, but they cannot be dried at higher temperatures on account of their instability.

The analysis was carried out as previously described in the case of the platinum salts (compare Abstr., 1881, 514), except as regards the estimation of the osmium in the potassium osmiochloride; these determinations were made by first reducing the salt in a stream of hydrogen, and then igniting the mixture of metal and potassium chloride in a platinum boat in a platinum tube in a stream of hydrogen, until the whole of the potassium chloride is volatilised.

The average of the 16 analyses of the potassium salt gives $Os = 190{\cdot}3$ $(O = 15{\cdot}96)$. The two determinations of the percentage of metal in the ammonium salt gave $Os = 190{\cdot}76$; as this result is, in all probability, too high, owing to the presence of oxychloride in the salt employed, it may be neglected. The atomic weight of osmium is, therefore, to be taken as 190·3; its true value is not known within about 0·2 per cent., but it is certainly less than that of iridium.

F. S. K.

Atomic Weights of the Platinum Metals. By K. Seubert (*Annalen*, **261**, 272—279; compare Abstr., 1888, 1043).—The latest determinations of the atomic weights of gold, and of the metals of the platinum group account for the anomalies previously observed in the classification of these metals according to the natural system; the order in which they are now to be placed is the following:—

Ruthenium	101·4	Rhodium	102·7
Osmium	190·3	Iridium	192·5
Palladium	106·35	Silver............	107·66
Platinum	194·3	Gold	196·7

F. S. K.

Mineralogical Chemistry.

Aurichalcite. By S. L. PENFIELD (*Amer. J. Sci.*, **41**, 106—109).—As some question still exists regarding the composition of aurichalcite, the author has analysed a specimen of unusual purity from an unknown locality in Utah. The mineral occurs in small, flattened, prismatic crystals in narrow seams in an impure limonite. Analysis gave the following results:—

CO_2.	CuO.	ZnO.	H_2O.	CaO.	Total.	Sp. gr.
16·50	20·88	52·18	9·91	0·86	100·33	3·52

The formula is $2RCO_3,3R(OH)_2$, in which R is Zn and Cu. This is the same as that proposed by Böttger in the original description of aurichalcite from the Altai. B. H. B.

Powellite, a New Mineral Species. By W. H. MELVILLE (*Amer. J. Sci.*, **41**, 138—141).—This new mineral was found with bornite at a mine in Western Idaho, in crystals belonging to the pyramidal system, closely allied in habit and development to scheelite. It has a yellow colour, a hardness of 3·5, and a sp. gr. of 4·526. Analysis yielded:—

MoO_3.	WO_3.	SiO_2.	CaO.	MgO.	Fe_2O_3.	Total.
58·58	10·28	3·25	25·55	0·16	1·65	99·47

Calcium molybdate has never before been observed in nature. It fills a gap existing in the series of isomorphous minerals, of which scheelite is the type. The new mineral is named in honour of the Director of the U.S. Geological Survey. B. H. B.

Columbite and Tantalite from the Black Hills of South Dakota. By W. P. HEADDEN (*Amer. J. Sci.*, **41**, 89—102).—Since 1884, when the occurrence of columbite in the Black Hills was first noticed, the mineral has been found at a number of localities in Pennington Co., and in the Nigger Hill district in Lawrence Co. The author gives the results of analyses of specimens of columbite from different localities in the Black Hills. In eight specimens from the Etta mine, the amount of tantalite increases with the specific gravity. This emphasises the fact that these various isomorphous mixtures not only occur at the same locality, but may even form the individual members of groups of crystals. They all have the form of columbite, but the ratio of Nb : Ta gradually changes from 6 : 1 to 6 : 2. Of the 20 specimens analysed, 7 of them contain the Nb and Ta in the ratio of 3 : 2, 4 in the ratio of 1 : 1, and 1 in the ratio of 1 : 1¼. The well-known tantalite from North Carolina gives the formula $6RTa_2O_6 + 4RNb_2O_6$, while the columbite from Northfield, Massachusets, and from the Yolo mine, South Dakota, gives the formula $5RTa_2O_6 + 4RNb_2O_6$. If these specimens are real tantalites and columbites respectively, there is an overlapping of specific gravity and chemical composition which destroys their value as guides in determining these minerals, when the columbite and tantalite molecules are nearly equal in number. There is probably, chemically, no sharp line between them; but the author has so far been unable to determine the superior limit of tantalic acid compatible with the columbite form.

A mineral from Turkey Creek, Colorado, gave, on analysis, the following results:—

Nb_2O_5.	Ta_2O_5.	SnO_2.	FeO.	MnO.	CaO.	WO_3.
73·45	2·74	0·21	11·32	9·70	0·61	1·14

This is an almost typical columbite, but is, like the Dakota columbites, rich in manganese.

Manganese columbite occurs on the Advance Claim, in Pennington Co., South Dakota, in a vein of granite. It has a sp. gr. of 6·170. An analysis of one of the largest crystals gave the following results:—

Nb_2O_5.	Ta_2O_5.	SnO_2.	FeO.	MnO.	Total.
47·22	34·27	0·32	1·89	16·25	99·95

B. H. B.

Artificial Formation of Amphibole. By K. CROUSTCHOFF (*Compt. rend.*, **112**, 677—679).—The following substances are introduced successively into glass flasks: an aqueous solution of dialysed silica, containing 3 per 100, an aqueous solution of dialysed aluminium hydroxide, an aqueous solution of dialysed ferric hydroxide, ferrous hydroxide, lime-water, magnesium hydroxide suspended in water, and a small quantity of a solution of potassium and sodium hydroxides. The flasks are then made vacuous, and are sealed up and heated at 550° for three months. The glass is strongly attacked, and on the sides of the flask are seen small, very brilliant, almost black, flattened prisms of hornblende, with the face (010) predominant, (110) often well developed, and (100) and (011) sometimes distinctly visible, the angle (011) (011) being 148° 28′. The optical sign is negative, the extinction (001) (010) = 17° 56′, and the polychroism is not intense. The crystals had the composition:—

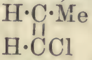
SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	Loss.
42·35	8·11	7·91	10·11	14·33	13·21	2·18	1·87	0·91 = 100·98

Four other minerals were formed at the same time, namely, small, pale-green prisms, which seem to be a pyroxene; colourless, isotropic, rounded grains of a zeolite; small, distinct, limpid crystals of quartz; thin, colourless, rhombic lamellæ, with the optical properties of orthose (adularia). C. H. B.

Organic Chemistry.

The Reaction Capacity of Chlorotrimethylene and some Allied Compounds. By G. GUSTAVSON (*J. pr. Chem.* [2], **43**, 396—402).—The author has isolated *chlorotrimethylene* from the product of the action of chlorine on trimethylene; it is a liquid of pleasant, sweet odour, lighter than water, in which it is insoluble, and boils at 43° (744 mm.); it is to be treated of in a future communication.

Chlorotrimethylene and dichlorotrimethylene were sealed up in tubes with bromine in the proportions $C_3H_5Cl + Br_2$ and $C_3H_4Cl_2 + Br_2$, after the manner previously described by the author (*Ann. Chim. Phys.* [5], **2**). Several such tubes were prepared and kept in the dark at 16—18°; from time to time a tube was broken by being shaken in a stoppered vessel containing potassium iodide solution, the liberated iodine was estimated, and the amount of uncombined bromine remaining in the tube thus determined. In this way the progress of the two reactions could be watched under similar conditions. The results given show that chlorotrimethylene combines more rapidly with bromine under these conditions than dichlorotrimethylene does; thus, after 81 days, 31·63 per cent. of bromine was still uncombined in the chlorotrimethylene tube, while, after 84 days, 51·32 per cent. remained uncombined in the dichlorotrimethylene tube; moreover, in the former only 1·2 per cent. of the bromine which had disappeared was found as hydrogen bromide, whereas as much as 12 per cent. was so found in the latter. Similar experiments with trimethylene showed that it combines more rapidly with bromine than either of the above chloro-substitution products.

Wislicenus has shown (*Annalen*, **248**, 308) that of the two chloropropylenes that which has the formula  $\begin{matrix}\text{H}\cdot\text{C}\cdot\text{Me}\\ \|\\ \text{H}\cdot\text{CCl}\end{matrix}$ is much more stable towards alcoholic potash than its isomeride; the author has treated chlorotrimethylene and allyl chloride under similar conditions with alcoholic potash, and finds that the former is much more stable towards this reagent than the latter. All the experiments hitherto made show that of the isomerides of the formula C_3H_5Cl chlorotrimethylene is the most stable towards alcoholic potash.

Chlorotrimethylene is somewhat more easily decomposed by water than dichlorotrimethylene. A. G. B.

Dimolecular Ethyl Cyanide. By P. S. BURNS (*J. pr. Chem.* [2], **43**, 406—408; compare Abstr., 1889, 114, 577).—*Benzoylimidopropionylethyl cyanide*, COPh·N:CEt·C_2H_4·CN, is obtained by warming a mixture of benzoic chloride with imidopropionylethyl cyanide, in molecular proportion, in ether on the water-bath, evaporating the ether, neutralising the aqueous solution of the residue with ammonia, and recrystallising the precipitate from alcohol; it forms beautiful needles melting at 198°, and sparingly soluble in cold alcohol and ether. The *hydrochloride* crystallises in slender needles.

α-Imidopropionylbenzoylethyl cyanide, $NH\!:\!CEt\cdot CMe(CN)\cdot COPh$, isomeric with the above, is obtained when the product of the action of sodium on ethyl cyanide, that is, the mixture of NaCN and $C_6H_9NaN_2$, is suspended in light petroleum and acted on by benzoic chloride; it separates from the filtrate as a pale-yellow oil. It is decomposed by hydrochloric acid, and this proves that it is not identical with the foregoing compound.

When phthalic anhydride is melted with imidopropionylethyl cyanide in molecular proportion, phthalimide and propionylethyl cyanide (α-cyanodiethyl ketone) are formed.

Oximidopropionylethyl cyanide, $NOH\!:\!CEt\cdot CHMe\cdot CN$, obtained by shaking the aqueous solutions of hydroxylamine and imidopropionylethyl cyanide, in molecular proportion, and extracting with ether, crystallises in slender needles, and melts at 42°. The *hydrochloride* and *zincochloride* were obtained. A. G. B.

Boiling Point of Diisopropylcarbinol. By G. POLETAEFF (*Ber.*, **24**, 1308—1314).—Diisopropyl ketone, prepared by the distillation of calcium isobutyrate, does not reduce ammoniacal silver solution, as stated by Münch. Diisopropylcarbinol is best obtained from the ketone by treatment with sodium amalgam in considerable excess; the liquid is at first cooled, but, as the reaction approaches completion, the application of heat is necessary; the operation extends over two months. The alcohol boils at 140° under a pressure of 760 mm.; not at 131·5°, as stated by Münch. The sp. gr. is 0·8445 at 0°/4°, and the coefficient of expansion between 0° and 20° = 0·00094; the refractive index for H_α 1·42047, and for $H_\gamma = 1·43156$. On oxidation with chromic anhydride, diisopropyl ketone, isobutyric acid, acetone, and acetic acid are formed. *Diisopropylcarbinyl acetate* is prepared by heating the alcohol with acetic anhydride in a sealed tube for 12 hours at 120°; it boils at 159·7° under a pressure of 752 mm., has a sp. gr. of 0·8856 at 0°/4°, and an expansion coefficient, from 0—20°, of 0·00101. The alcohol is regenerated by heating with alcoholic potash.

Applying the above boiling point to the expression $MeOH + 2Pr^\beta OH - CHPr^\beta_2\cdot OH = 2H_2O$, that is to say, $60° + (82·8 \times 2) - 140° = 85·6°$, 42·8° is obtained as the equivalent for 1 mol. of water; the value previously obtained from methylisopropylcarbinol is 40·3°, therefore 41·5°, the mean of these two numbers, may be considered to be the constant for calculating the boiling point of secondary alcohols with secondary radicles. J. B. T.

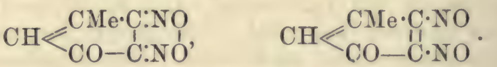
Eulyte. By A. ANGELI (*Ber.*, **24**, 1303—1305).—Eulyte, $C_6H_6N_4O_7$, which is formed by the action of nitric acid on citraconic acid, is not altered by treatment with acetic anhydride and benzoic chloride, or with hydroxylamine or phenylhydrazine. When heated with sulphuric acid, or hydrochloric acid, under pressure, decomposition takes place; by the action of alkalis at the ordinary temperature, nitrous acid is eliminated, and on the addition of iodine to the solution, iodoform is deposited in considerable quantity.

By the distillation of eulyte with hydrogen potassium sulphate and a little powdered pumice, nitrous fumes are evolved, and a yellow, viscid liquid is obtained; this is probably a *diketone* of the formula $C_6H_6N_2O_6$; it does not react with orthophenylenediamine. On treatment with phenylhydrazine in dilute acetic acid solution, a *diphenylhydrazone*, $C_{18}H_{18}N_6O_4$, is deposited, which crystallises from alcohol in orange-yellow plates melting at 110—111°. J. B. T.

Solvent for Cellulose. By C. F. Cross and E. J. Bevan (*Chem. News*, **63**, 66).—The authors find that, by dissolving zinc chloride in twice its weight of hydrochloric acid, a solution of sp. gr. 1·44 is obtained, which dissolves cellulose instantly without sensible modification, and hence provides a useful solvent, especially suitable for the chemical or microscopical investigations of the vegetable fibres.

D. A. L.

Action of Nitric Acid on Acetonylacetone. By A. Angeli (*Ber.*, **24**, 1305—1306).—On warming acetonylacetone with 5 parts of concentrated nitric acid, an energetic reaction occurs, and, on cooling, large, colourless crystals are deposited which melt at 128—129°. The compound has the formula $C_6H_4N_2O_3$, and is readily soluble in benzene, acetone, or ethyl acetate; it is not acted on by alkaline carbonates, but dissolves in aqueous alkalis with a yellow colour, and does not give the nitroso-reaction. The *phenylhydrazone*, $C_6H_4N_2O_2{:}N_2HPh$, crystallises from alcohol, on the addition of light petroleum, in small, yellow needles and melts at 161° with decomposition. The author suggests one or other of the following formulæ for the ketone:—



J. B. T.

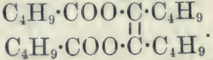
Dibutyryl and Di-isovaleryl. By H. Klinger and L. Schmitz (*Ber.*, **24**, 1271—1276).—The results of the investigation of the constitution of isobenzile, which have shown it to be diphenylacetylene benzoate (this vol., p. 931), make it probable that the supposed dibutyryl of Freund (*Annalen*, **118**, 33) and the di-isovaleryl of Brühl (Abstr., 1879, 520) have a similar constitution. It has already been pointed out by V. Meyer that they cannot be really α-diketones, as they are colourless substances (*Ber.*, **21**, 809, footnote). The authors have, therefore, re-examined these compounds, and the results already obtained show that in all probability they are also ethereal salts of glycols.

Dibutyryl was obtained in the manner described by Münchmeyer (Abstr., 1886, 350), namely, by acting on an ethereal solution of butyric chloride with sodium wire. It is obtained as an oil, and boils at 155—165° under a pressure of 12 mm. On warming with alcoholic potash, it yields butyric acid, and a yellowish oil which boils at 180—190° and has the composition $C_8H_{16}O_2$. This has in all probability the constitution $OH\cdot CHPr^{\alpha}\cdot COPr^{\alpha}$, and may be termed *butyroïn*. It combines with phenylhydrazine, forming a *hydrazone* crystallising in straw-yellow needles and melting at 135°. The supposed dibutyrylmonoxime obtained by Münchmeyer (*loc. cit.*) is probably butyroïnmonoxime. When butyroïn is boiled with aqueous potash in presence of air, it yields *dipropylglycollic acid*, $OH\cdot CPr^{\alpha}{}_2\cdot COOH$, just as benzoïn yields benzilic acid. The new acid crystallises from water in long, white needles, melts at 72—73°, and yields a *barium* salt,

$$[OH\cdot C_6H_{14}\cdot COO]_2Ba,$$

crystallising in white scales. From these results there can be little doubt that dibutyryl is in reality *dipropylacetylene dibutyrate*, $CH_3\cdot[CH_2]_2\cdot COO\cdot CPr^{\alpha}:CPr^{\alpha}\cdot OOC\cdot[CH_2]_2\cdot CH_3$.

Di-isovaleryl is obtained in a similar manner to dibutyryl from isovaleric chloride. It distils with slight decomposition at 155—165° under 12 mm. pressure, and is resolved by alcoholic potash into valeric acid and an oil which boils at 85—95° under a pressure of 12 mm., has the composition $C_{10}H_{20}O_2$, and is in all probability *isovaleroïn*, $C_4H_9\cdot CO\cdot CH(OH)\cdot C_4H_9$. It combines with phenylhydrazine, and on heating with potash in presence of air, forms a new acid, apparently *di-isobutylglycollic acid*, $OH\cdot C(C_4H_9)_2\cdot COOH$, which crystallises from water in long, white needles melting at 114°. Hence it appears that di-isovaleryl is *di-isobutylacetylene di-isovalerate*,



$$\begin{array}{c} C_4H_9\cdot COO\cdot C\cdot C_4H_9 \\ \| \\ C_4H_9\cdot COO\cdot C\cdot C_4H_9 \end{array}.$$

H. G. C.

Angelic Acid. By E. SCHMIDT (*Arch. Pharm.* [2], **29**, 68—71).—Finding that a sample of angelic acid 25 years old was pure methylcrotonic acid, the author supposed that the conversion had come about simply by long keeping, especially as Demarçay (*Compt. rend.*, **10**, 83, 906) has shown that the application of heat causes the change. Further examination of other samples, even 50 years old, shows, however, that angelic acid can be preserved unchanged. Notwithstanding the assertions made in text-books that this acid exists in angelica root, either in the free state or as an ethereal compound from which distillation with water sets it free, it is probable that the acid is a decomposition product of some unknown compound occurring in the root. J. T.

Substitution Derivatives of Succinic Acid. By C. A. BISCHOFF (*Ber.*, **24**, 1064—1074).—No isomeride of succinic acid could be obtained by dissolving succinic anhydride in water at low temperatures. An attempt to isolate isomerides of methyl- and ethylsuccinic acids by fractional crystallisation from benzene and chloroform also gave negative results. In order to ascertain whether derivatives of glutaric acid are formed as secondary products in the preparation of substituted succinic acids from ethyl malonate, ethyl ethylpropenyltricarboxylate was prepared as formerly described (Abstr., 1890, 743), and then hydrolysed. No ethylglutaric acid was obtained, but the two symmetrical ethylmethylsuccinic acids were again found in the distillate, the anhydrides of these acids having very nearly the same boiling points. In the preparation of the two symmetrical diethylsuccinic acids also no glutaric acid was obtained. The anhydrides of these two acids have nearly the same boiling point. Attempts to obtain an optically active diethylsuccinic acid were not successful.

The author gives a list of the substitution products of succinic acids which have up to the present been prepared, together with their melting points. The monosubstitution derivatives all melt at 91—114°, the symmetrical di-derivatives at 115—138°, the asymmetrical dimethyl- and all tri-derivatives at 139—141°, the parasymmetrical di-derivatives at 154—197°, and tetramethylsuccinic acid at 200°. The only exceptions to this rule are the monobenzyl-, diphenyl-, and Zelinsky's mesoethylmethylsuccinic acid, and also succinic acid itself. H. C.

Theoretical Results of Studies in the Succinic Acid Group. By C. A. Bischoff (*Ber.*, **24**, 1074—1085).—To explain the isomerism of derivatives of succinic acid, the author formerly put forward a theory of dynamical isomerism (Abstr., 1890, 723), according to which the rotation of singly bound carbon atoms may be limited, owing to the vibrations of the atomic complexes in the molecule causing interference with one another. If this interference, or, as the author terms it, "collision," takes place between carboxyl groups, it will probably be attended with loss of water and the formation of an anhydride. On the other hand, collision between alkyl groups might result in limitation of the free rotation of the carbon atoms with which they were united, and the consequent occurrence of isomerides.

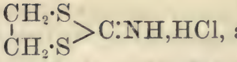
On the latter assumption, the occurrence of isomeric trimethylsuccinic acids, said to have been recently obtained by Zelinsky and Besredka, would be in perfect accordance with the theory. Careful consideration of Zelinsky and Besredka's results leads, however, to the conclusion that the isomeric trimethylsuccinic acid was in reality dimethylglutaric acid, and that up to the present only one trimethylsuccinic acid has been obtained. H. C.

Dynamical Hypothesis in its Application to the Succinic Acid Group. By C. A. Bischoff (*Ber.*, **24**, 1085—1095).—The dynamical hypothesis, explained in a former paper (Abstr., 1890, 723), is applied to the cases of isomerism among the succinic acid derivatives. It is necessary to assume with Wislicenus that carboxyl is repelled by carboxyl, with Baeyer that methyl is only slightly repelled or even attracted by methyl, and also that carboxyl repels methyl. The influence of the attraction of methyl or alkyl groups for one another would bring about a proximity of the carboxyl groups. From this would result the ready formation of anhydrides and increased conductivity noticed in the higher substituted succinic acids. If under any influence, such as that of a dehydrating agent, carboxyl were brought into proximity with carboxyl, and the agent then removed, the two carboxyl groups would repel one another, unless the counter-attraction of two alkyl groups for one another overcame the repulsion. This repulsion also would be counteracted by the tendency of an alkyl group to repel carboxyl, and therefore the separation of carboxyl from carboxyl could only be effected with difficulty. This explains the fact that asymmetrical dimethylsuccinic acid only exists in one modification, and trimethylsuccinic acid exists probably in two active enantiomorphic forms, the ordinary acid being a mixture of the two.

The further application of the hypothesis to the succinic acids is fully discussed by the author with the aid of diagrams. It has the advantage over that of Meyer and Riecke (Abstr., 1888, 549) that no assumptions are made as to so-called positive or negative groups, and the conception of affinity is as far as possible excluded in favour of a purely mechanical attraction or repulsion. H. C.

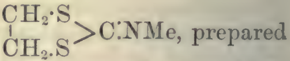
Oxidation Products of Brominated Thiophens. By G. Ciamician and A. Angeli (*Ber.*, **24**, 1347—1351).—The dibromomaleïc anhydride obtained from tetrabromothiophen and nitric acid (this vol., p. 427) melts at 117—118°, even after repeated distillation in a stream of dry carbonic anhydride and crystallisation from a mixture of benzene and light petroleum, whereas that obtained from maleïc acid melts at 114—115°. When the supposed dibromacetylacrylic acid prepared from α-tribromothiotolen (*loc. cit.*) is reduced with sodium amalgam in the presence of sulphuric acid, ether extracts an oily product which, on dissolving in chloroform and treating with bromine, yields a compound which crystallises from chloroform in colourless needles, melts at 114—115°, and has all the properties of dibromolevulinic acid. When tetrabromothiophen (3 grams) is dissolved in 90 per cent. acetic acid (50 c.c.), and boiled with chromic anhydride (5 grams), bromine is evolved, and a reddish-yellow, crystalline powder separates, which is very sparingly soluble in the ordinary solvents, and is purified by crystallisation from a large quantity of boiling xylene; it has the composition represented by the formula $C_9Br_4S_2O_2$, does not melt at 310°, but sublimes without decomposition when heated on platinum foil; it dissolves in alkalis with a brown colour, and hydrogen sulphide is evolved on heating with phenylhydrazine. A second compound separates in yellow flocks on adding light petroleum to the xylene filtrate from the red compound. A red compound closely resembling that above described is also obtained by treating α-tribromothiotolen with chromic anhydride. When αα′-dibromothioxylen and αα′-methylphenyltribromothiophen are oxidised with nitric acid, semi-solid or amorphous substances are formed whose purification is difficult; better results may, however, be obtained by varying the conditions of the experiments.

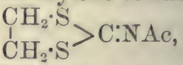
The concluding portion of the paper is devoted to a discussion of the configuration of thiophen, pyrroline, and furfuran. A. R. L.

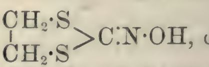
So-called Isothiocyanoethylsulphine. By A. Miolati (*Annalen*, **262**, 61—81).—The compound obtained by Glutz (*Annalen*, **153**, 313) by treating ethylenethiocarbimide with tin and hydrochloric acid, and named by him isothiocyanoethylsulphine chloride, has the constitution  $\begin{matrix}CH_2\cdot S\\ \vert\\ CH_2\cdot S\end{matrix}\!>C{:}NH,HCl$, and should therefore be called μ-imidomethylene ethylene bisulphide hydrochloride; its formation from ethylenethiocarbimide is most easily explained by assuming that an intermediate product of the constitution $SH\cdot CH_2\cdot CH_2\cdot S\cdot CO\cdot NH_2$ is first formed by the addition of 1 mol. H_2O.

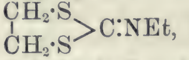
μ-Imidomethylene ethylene bisulphide hydrochloride is obtained when ethylenethiocarbimide is boiled for a long time with concentrated hydrochloric acid, but it is best prepared by heating ethylenethiocarbimide with excess of tin and concentrated hydrochloric acid; the *stannochloride*, $(C_3H_5S_2N)_2,H_2SnCl_4$, is deposited from the cold filtered solution, and can be purified by recrystallisation from hot water. The hydrochloride, obtained by decomposing the stannochloride with hydrogen sulphide and evaporating the filtered solution, crystallises from hot alcohol in nacreous scales, but it cannot be freed from ammonium chloride without considerable loss; the preparation employed in the experiments described below contained a little ammonium chloride. When the hydrochloride is oxidised with nitric acid of sp. gr. 1·52, it is converted into ethylenedisulphonic acid (m. p. 104°, corr.), and when treated with potassium carbonate, it yields ammonia and diethylene tetrasulphide.

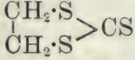
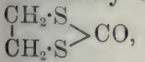
The free imidomethylene ethylene bisulphide can be obtained by shaking the hydrochloride with potassium carbonate and ether, and then evaporating the ethereal solution; it is a colourless oil, having a slight mercaptan-like odour, and it decomposes on exposure to the air, with formation of diethylene tetrasulphide. It is insoluble in water, gives with silver nitrate a colourless silver derivative, and is quickly decomposed by cold dilute alkalis. The *hydriodide*, $C_4H_7S_2N,HI$, is obtained when the hydrochloride of the base is warmed with methyl iodide in alcoholic solution; it crystallises in colourless needles, turns brown, and melts at 182—184° with complete decomposition, and is very readily soluble in water and hot alcohol.

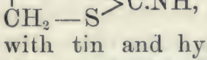
Methylimidomethylene ethylene bisulphide,  $\begin{matrix}CH_2\cdot S\\ \vert\\ CH_2\cdot S\end{matrix}\!>C{:}NMe$, prepared by decomposing the hydriodide with alkalis, is an oil; it quickly decomposes with evolution of methylamine, being converted into a colourless, amorphous compound, probably diethylene tetrasulphide.

Acetylimidomethylene ethylene bisulphide,  $\begin{matrix}CH_2\cdot S\\ \vert\\ CH_2\cdot S\end{matrix}\!>C{:}NAc$, is formed when the hydrochloride of the base is boiled with excess of acetic anhydride; it crystallises from alcohol and benzene in thin plates, melts at 69°, and is readily soluble in alcohol and benzene, but only sparingly in ether, and almost insoluble in water; it is decomposed by alkalis, and when warmed with benzoic chloride it is converted into a crystalline compound, probably the benzoyl derivative, which melts at 141—143°.

Oximidomethylene ethylene bisulphide,  $\begin{matrix}CH_2\cdot S\\ \vert\\ CH_2\cdot S\end{matrix}\!>C{:}N\cdot OH$, can be obtained by warming the hydrochloride with hydroxylamine hydrochloride in faintly alkaline solution, and then allowing the filtered solution to cool; it crystallises in long, colourless needles, melts at 126° (corr.), and is almost insoluble in cold water, but readily soluble in hot water, alcohol, glacial acetic acid, alkalis, and acids; it is not decomposed by boiling concentrated hydrochloric acid. The *hydrazone*, $C_9H_{10}S_2N_2$, prepared by warming an aqueous solution of the hydrochloride with phenylhydrazine hydrochloride and sodium acetate, and then adding sodium carbonate, crystallises from hot alcohol in greyish plates, melts at 88°, and is insoluble in hot water, and only sparingly soluble in ether, but readily in alcohol.

Ethylimidomethylene ethylene bisulphide,  $\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CH_2{\cdot}S\end{array}\right>C{:}NEt$, is formed when a 33 per cent. solution of ethylamine is added, drop by drop, to a hot, concentrated solution of the hydrochloride of the base; after boiling until the evolution of ammonia is at an end, and then adding stannous chloride, the stannochloride $(C_5H_9S_2N)_2,H_2SnCl_4$, is deposited in crystals. The stannochloride of the *allyl* derivative was prepared in like manner; it has the composition $(C_6H_9S_2N)_2,H_2SnCl_4$. The *paratolyl* derivative is precipitated as an oil on treating a solution of the imido-base with paratoluidine; the *hydrochloride*, $C_{10}H_{11}S_2N,HCl$, separates from ether in colourless needles, melts at about 168° with decomposition, and is decomposed by water. The *parahydroxyphenyl* derivative, prepared by treating a solution of the imido-base with paramidophenol, separates from hot alcohol in large, dirty-brown crystals, melts at 204—205°, and is soluble in alkalis, but insoluble in acids.

When the hydrochloride of the imido-base is dissolved in alcoholic carbon bisulphide, and the solution gradually treated with alcoholic potash, ethylene thiocarbonate,  $\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CH_2{\cdot}S\end{array}\right>CS$ (m. p. 40—41°, corr.), is formed; when this substance is treated with hydroxylamine, it is converted into the oxime described above, and on oxidation with moderately dilute nitric acid, it yields ketomethylene bisulphide,  $\left.\begin{array}{l}CH_2{\cdot}S\\ |\\ CH_2{\cdot}S\end{array}\right>CO$, and not ethylene thioxycarbonate, as was supposed by Husemann (*Annalen*, **123**, 83).

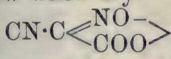
μ-Imidomethylene propylene bisulphide,  $\left.\begin{array}{l}CHMe{\cdot}S\\ |\\ CH_2-S\end{array}\right>C{:}NH$, is formed when propylenethiocarbimide is boiled with tin and hydrochloric acid; the *stannochloride*, $(C_4H_7S_2N)_2,H_2SnCl_4$, crystallises from water in plates, and is readily soluble. The *hydrochloride*, $C_4H_7S_2N,HCl$, forms well-defined plates, melts at 172—175°, and is readily soluble in water. The *acetyl* derivative, $C_6H_9S_2NO$, prepared by boiling the hydrochloride with acetic anhydride, is a crystalline powder which melts at 59·5°, and is almost insoluble in water and ether, but very readily soluble in alcohol.

When trimethylenethiocarbimide is boiled with tin and hydrochloric acid, it yields trimethylenemercaptan, and not imidomethylenetrimethylene bisulphide. F. S. K.

Preparation of Pyromucic Acid from Furfuraldehyde. By J. VOLHARD (*Annalen*, **261**, 379—380).—A better method for the preparation of pyromucic acid than that described by Schiff (compare this vol., p. 676) is to oxidise furfuraldehyde with potassium permanganate. For this purpose furfuraldehyde (9·6 grams) is mixed with water (400 c.c.) and potassium hydroxide (26 grams), and a solution of potassium permanganate (10·5 grams) in water (400 c.c.) gradually added, the temperature being kept below 20°; the solution is then boiled, filtered, the filtrate evaporated to a small volume, mixed with hydrochloric acid, and extracted with ether. The yield of the crude acid is about 8·9 grams; it is most easily obtained in a pure condition by sublimation, the acid being heated at 130—140° in a glass tube through which is passed a stream of air under a pressure of about 50—60 mm. F. S. K.

Furazancarboxylic Acid. By L. WOLFF and P. F. GANS (*Ber.*, **24**, 1165—1172).—Diisonitrosovaleric acid, when treated with concentrated sulphuric acid, loses a molecule of water, and is converted into furazanpropionic acid. The latter, under the action of cold sodium hydroxide or ammonia, is converted into the isomeric cyanonitrosobutyric acid, $CN\cdot C(:NOH)\cdot CH_2\cdot CH_2\cdot COOH$, and on oxidation it yields furazancarboxylic acid, which is converted by alkali into cyanonitrosoacetic acid.

Furazancarboxylic Acid.—The oxidation of furazanpropionic acid by means of potassium permanganate is a somewhat difficult operation, as the action either goes too far, or not far enough, unless special care is taken. The following conditions give a good yield. Furazanpropionic acid (2 grams) is dissolved in a mixture of concentrated sulphuric acid (20 grams) and water (100 c.c.), heated at 85—90°, and mixed with a hot saturated solution of permanganate (20 grams) in four portions. The oxidation at first proceeds rapidly, afterwards more slowly, and is complete in 8—9 hours. The acid is extracted with ether, and purified by crystallisation from benzene. It is very easily soluble in water, ether, and alcohol, somewhat easily in boiling chloroform and benzene, and sparingly in carbon bisulphide and light petroleum. From benzene, it crystallises in long leaflets or needles of satiny lustre, and melts at 107° to a colourless oil. It dissolves in aqueous alkalis with a deep yellow coloration, and is immediately converted into the isomeric cyanonitrosoacetic acid; on boiling with water it is slowly decomposed with formation of hydrocyanic acid. The aqueous solution reddens litmus, and with carbonates yields well characterised salts, which are unstable to boiling water. The *calcium* salt, $(C_3HN_2O_3)_2Ca + H_2O$, obtained by saturating the cold acid solution with calcium carbonate, crystallises in small needles, and is easily soluble in water. By boiling the aqueous solution, it is slowly converted into calcium cyanonitrosoacetate, hydrocyanic acid being formed at the same time. The *silver* salt, $C_3HN_2O_3Ag$, is obtained as a white, crystalline precipitate on adding silver nitrate to a solution of the calcium salt. It dissolves somewhat easily in boiling water, crystallises in shining needles, and decrepitates when quickly heated. By prolonged boiling with water, it is converted into a sparingly soluble, yellow crystalline salt.

Cyanonitrosoacetic acid, $NC\cdot C(NOH)\cdot COOH$, is obtained by treating furazancarboxylic acid with excess of sodium hydroxide, strongly acidifying the solution with sulphuric acid, and extracting with ether. The acid is purified by crystallisation from a mixture of benzene and ether, and then from water. It is very easily soluble in water, ether, and alcohol, sparingly so in benzene, petroleum, and carbon bisulphide, crystallises in colourless prisms containing $\frac{1}{2}$ mol. H_2O, and melts at 103°. The anhydrous acid melts at 129° with violent frothing, and is converted into a crystalline compound, which is probably cyanuric acid. The aqueous solution reacts strongly acid; with ferric chloride it gives a red coloration, which disappears on the addition of a mineral acid. When boiled with water, it evolves hydrocyanic acid, and when boiled with potassium hydroxide, is converted into ammonia and nitrosomalonic acid. Towards alkaline carbonates it behaves as a bibasic acid, and yields salts of the formula $NC\cdot C(\colon NOM)\cdot COOM$, which are yellow when dry. The acid salts are colourless. The *normal calcium* salt,  $CN\cdot C{<}\begin{smallmatrix}NO-\\ COO\end{smallmatrix}{>}Ca + 7H_2O$, is obtained by saturating an aqueous solution of the acid with calcium carbonate, and evaporating over sulphuric acid. It crystallises in colourless, six-sided tablets, and is easily soluble in hot water, less so in cold water. When dried in a desiccator, it loses 4 mols. H_2O, and is converted into a lemon-yellow powder; the remaining water of crystallisation is not lost at 100°, and at a higher temperature the salt turns brown. The yellow salt takes up water to form the colourless salt, and dissolves in water to a yellow solution, which, on the addition of ferric chloride, turns deep red. The *normal silver* salt is obtained as a yellow, crystalline precipitate on adding silver nitrate to a solution of the normal calcium salt. It is sparingly soluble in water, easily so in excess of nitric acid or ammonia, and decrepitates when gently heated. The *acid* salt, $C_3HN_2O_3Ag$, is obtained by careful addition of nitric acid to the normal salt, and also as a white crystalline precipitate by adding silver nitrate to an aqueous solution of the free acid. It crystallises from boiling water containing nitric acid in long, colourless needles, decrepitates when heated, and is converted by prolonged boiling with water, more easily by warming with ammonia, into the yellow normal salt.

Nitrosomalonic acid is obtained in theoretical quantity by boiling 1 part of cyanonitrosoacetic acid or furazancarboxylic acid with potash (2 parts) and water (6 parts) in a reflux apparatus as long as ammonia is evolved. It melts at 139°, decomposes when strongly heated, with a hissing sound, and on heating in aqueous solution, decomposes into carbonic anhydride, hydrocyanic acid, and water. It has the properties ascribed to it by Baeyer (*Annalen*, **131**, 292). E. C. R.

Constitution of Benzene. By A. Claus (*J. pr. Chem.* [2], **43**, 321—343).—A reply to Zincke's paper in *Annalen*, **261**, 208, as far as it concerns the author's diagonal formula for benzene.

A. G. B.

Cymene. By O. Widman (*Ber.*, **24**, 1362—1363).—A reply to R. Meyer (this vol., p. 688).

Oxidation of Cymene and Isopropylbenzene by Chromyl Chloride. By W. v. Miller and Rohde (*Ber.*, **24**, 1356—1362).—The authors obtained an aldehyde on treating cymene with chromyl chloride (Abstr., 1890, 978), and this was likewise obtained by Errera (*ibid.*, 1254), together with a second compound which he has recently shown to be paratolyl methyl ketone (*Gazzetta*, **21**, 65). They now find that, under similar conditions, isopropylbenzene yields hydratropaldehyde and acetophenone.

Hydratropaldehyde, $C_9H_{10}O$, is obtained from that portion of the product which combines with sodium hydrogen sulphite. It is an almost colourless oil, having an odour resembling that of the aldehyde obtained from cymene, and boils at 203—204° (thermometer in the vapour) under a pressure of 716 mm.; it colours a sulphurous acid solution of rosaniline, reduces an ammoniacal silver solution in the cold, and gives an oily compound with phenylhydrazine; it does not appear to oxidise, or only does so very slowly, in the air. Taking the above in conjunction with Widman's recent discovery (this vol., p. 686) that cymene is paramethylisopropylbenzene, there can be no doubt that the aldehyde obtained from the latter is paramethylhydratropaldehyde as suggested (*loc. cit.*). A. R. L.

Action of Halogens on Aromatic Compounds in presence of Light. By J. Schramm (*Ber.*, **24**, 1332—1337).—By the action of bromine on parethyltoluene in molecular proportion in sunlight, 1 atom of hydrogen in the ethyl group is displaced; the resulting product is liquid, and readily decomposes on distillation or by treatment with potash, paramethylcinnamene being obtained. The latter combines directly with 1 mol. of bromine to form *paramethylcinnamene dibromide*, $C_6H_4Me{\cdot}CHBr{\cdot}CH_2Br$, which crystallises from alcohol in long, slender needles melting at 44·5°. The same substance may be more readily prepared by heating the above liquid bromo-derivative with 1 mol. proportion of bromine on the water-bath in darkness.

Parethyltoluene also reacts with 2 mol. proportions of bromine in sunlight; the product is liquid and probably consists of paramethyl-β-cinnamene dibromide. Ethylbenzene may be readily prepared by the interaction of benzene, ethyl bromide, and aluminium chloride, at 0°; on treating the crude product with 1 mol. proportion of bromine in sunlight, and afterwards with the same quantity in darkness at higher temperatures, *parabromocinnamene dibromide*, $C_6H_4Br{\cdot}CHBr{\cdot}CH_2Br$, is formed, crystallising from alcohol in long, slender needles melting at 60°; the compound is identical with that obtained by the addition of bromine to parabromocinnamene, and yields parabromobenzoic acid on oxidation. By boiling with aqueous potassium carbonate solution, *parabromophenylethylene glycol* is formed; this crystallises from benzene or water in needles, melts at 102°, and readily decolorises potassium permanganate solution.

Bromopropylbenzene behaves towards bromine like the corresponding ethyl derivative. *Parabromo-αβ-dibromopropylbenzene*,

$$C_6H_4Br{\cdot}CHBr{\cdot}CHMeBr,$$

crystallises from alcohol in lustrous needles and melts at 61°; long, prismatic crystals are deposited on slowly evaporating a dilute alcoholic solution.

Parabromobutylbenzene is prepared by the action of bromine on butylbenzene in presence of iodine, and boils at 240—242°. It reacts with bromine in a manner similar to the propyl and ethyl derivatives, and yields *parabromo-β-γ-dibromobutylbenzene*,

$$C_6H_4Br.CHBr{\cdot}CHEtBr,$$

which crystallises from alcohol in highly lustrous plates and melts at 76·5°. J. B. T.

Thymol. By A. CLAUS and E. KRAUSE (*J. pr. Chem.* [2], **43**, 344—355).—Engelhardt and Latschinoff's α-thymolsulphonic acid is the para-acid, as they themselves showed by oxidising it to thymoquinone (this Journal, 1871, 1053); their β-acid has been shown by the authors to be thymolorthosulphonic acid; the γ-acid is, therefore, thymolmetasulphonic acid.

Orthobromothymolparasulphonic acid (brom-α-sulphothymolic acid of Engelhardt and Latschinoff)

$$[OH : Br : Me : SO_3H : Pr = 1 : 2 : 3 : 4 : 6]$$

is best obtained by adding a solution of bromine (1 mol.) in three times its weight of glacial acetic acid, by drops, to an aqueous solution of potassium thymolparasulphonate with continuous shaking; the liquid is then neutralised with potash and evaporated. The free acid cannot be crystallised by evaporation over the water-bath, as, after a certain degree of concentration, it decomposes into bromothymol and sulphuric acid; over sulphuric acid it crystallises in small, colourless columns (with 1 mol. H_2O) which melt in their water of crystallisation at 55° (uncorr.). The *potassium* (with 1 mol. H_2O), *sodium* (with 2 mols. H_2O), the *barium*, the *lead* (with 3 mols. H_2O), and the *silver* salts are described.

Orthobromothymol [OH : Pr : Br : Me = 1 : 6 : 2 : 3] separates as an oily layer when potassium orthobromothymolparasulphonic acid is heated with dilute hydrochloric acid in a tube at 150°. It is a clear, yellow oil which boils at 240° (uncorr.) undecomposed, and does not solidify in a freezing mixture.

2-Bromothymoquinone [O_2 : Br : Me : Pr = 1 : 4 : 2 : 3 : 6] is obtained when orthobromothymolparasulphonic acid is oxidised with chromic acid; it crystallises in beautiful, red, prismatic columns which melt at 48° (uncorr.); it is identical with the bromothymoquinone obtained by action of hydrogen bromide on thymoquinone (compare Kehrmann, Abstr., 1890, 367). The action of concentrated nitric acid on orthobromothymolparasulphonic acid yields orthoparadinitrothymol (m. p. 54—55°, uncorr.).

The *potassium* (with 1 mol. H_2O), *barium* (with 4 mols. H_2O), *silver* (with 2 mols. H_2O), *copper*, *nickel*, and *cobalt* salts of thymolorthosulphonic acid are described. *Potassium parabromothymolorthosulphonate* [OH : Pr : Br : Me : SO_3K = 1 : 6 : 4 : 3 : 2] is obtained by the action of bromine on potassium thymolorthosulphonate; the *barium* salt is described; the free acid cannot be crystallised, being so easily decomposed into sulphonic acid and *parabromothymol*, which is a clear yellow oil; by the action of bromine it yields orthoparadibromothymol, which is characterised by its oxidation into 2-bromothymoquinone.

The authors doubt whether Mazzara's bromothymol is the para-compound (Abstr., 1890, 602, 753, 884); investigations are being made into this question. A. G. B.

Action of Sunlight on Organic Compounds. By H. KLINGER and O. STANDKE (*Ber.*, **24**, 1340—1346; compare Abstr., 1886, 888; 1889, 405).—When a mixture of finely powdered quinone (5 grams) and benzaldehyde (10 c.c.) is exposed in a sealed tube to direct sunlight, the yellow solution becomes darker, and greenish-black crystals separate, which increase in quantity as the quinone dissolves. No pressure is observed on opening the tube; the crystals are collected, washed with ether, and, after crystallising from dilute alcohol, identified as quinhydrone. *Dibenzoylquinhydrone*, $C_{32}H_{24}O_8$, is obtained when the filtrate and ethereal washings from the quinhydrone are allowed to evaporate in the sun. The black, semi-crystalline residue is spread upon a porous tile, and dissolved in dilute alcohol, when it separates in long, black, flat needles, having a bluish-violet lustre, and a brown colour by transmitted light; it melts at 116—117°, and dissolves in alcohol, ether, and benzene, with a yellow colour, splitting up into its components (see below); heated with water, it melts, the brown drops gradually become lighter, and quinone passes off with the steam.

Benzoylquinol (*dihydroxybenzophenone*), $C_6H_3Bz(OH)_2$, is obtained, together with quinol, when dibenzoylquinhydrone is heated with sulphurous acid; it separates in yellow oily drops which solidify on cooling, whereas quinol remains in solution; it forms long, yellow needles from dilute alcohol, and is very readily soluble in ether, benzene, and alcohol; it melts at 125°, and yields dibenzoylquinhydrone when a dilute alcoholic solution is mixed with one of quinone. The *tribenzoyl derivative*, $C_6H_3Bz(OBz)_2$, which crystallises from alcohol in glistening, white needles, melts at 118°, and is sparingly soluble in cold alcohol, readily in ether and benzene, is formed on treating benzoylquinol with benzoic chloride; by hydrolysis with alcoholic potash, benzoylquinol is regenerated.

Isovaleroquinhydrone, $C_{17}H_{18}O_5$, is formed together with quinhydrone from quinone and isovaleraldehyde; it crystallises from dilute alcohol in beautiful, red tables with a metallic lustre, which gradually undergo change in the air and become yellow; it dissolves with a yellow colour in alcohol, ether, benzene, and glacial acetic acid, and melts at 103°.

Isovaleroquinol, $C_4H_9{\cdot}CO{\cdot}C_6H_3(OH)_2$, is obtained, together with quinol, when isovaleroquinhydrone is treated with sulphurous acid; it separates from dilute alcohol in yellow needles, and from benzene, in prisms, which become dull in the air, melts at 115°, and dissolves in alkalis with a yellowish-red colour; it combines with quinone to form isovaleroquinhydrone; the *dibenzoyl derivative*, $C_4H_9{\cdot}CO{\cdot}C_6H_3(OBz)_2$, crystallises from alcohol in white needles, melts at 105°, and yields isovaleroquinol on hydrolysis.

The above-mentioned aldehydes have scarcely any action on quinone in the dark, less quinhydrone being formed after a month's action than by an hour's exposure to light. A. R. L.

Action of Aniline on Chloride and Bromide of Arsenic. By R. ANSCHÜTZ and H. WEYER (*Annalen*, **261**, 279—297).—*Arsenanilidodichloride*, $AsCl_2 \cdot NHPh$, is formed, with development of heat, when a dry ethereal solution of aniline (1 mol.) is gradually added, with constant shaking, to a dry ethereal solution of pure arsenic trichloride; the mixture is boiled for some time, then allowed to cool, and the intense yellow solution of the arsenic compound separated from the precipitated aniline hydrochloride, moisture being carefully excluded. The solution is partially evaporated on the water-bath, and then kept over phosphoric anhydride, when a crystalline mixture of arsenanilidodichloride, aniline hydrochloride, and arsendianilidochloride is deposited; the first-named compound can be isolated in a pure condition by repeated recrystallisation from ether, in which the two impurities are very sparingly soluble; the yield is very small. Arsenanilidodichloride is a yellow, crystalline powder; it melts at 87—88°, decomposes at a higher temperature, and is readily soluble in warm ether and chloroform, but only very sparingly in benzene; it quickly decomposes on exposure to moist air, being converted into arsenious oxide, hydrochloric acid, and aniline hydrochloride.

Arsendianilidochloride, $AsCl(NHPh)_2$, can be prepared by gradually adding an ethereal solution of arsenic trichloride (1 mol.) to an ethereal solution of aniline (6 mols.); as soon as the reaction is at an end, the colourless solution is separated from the precipitated aniline hydrochloride and allowed to cool, when the arsenic compound is deposited in transparent, rhombic crystals, which immediately become cloudy on exposure to the air. It is purified by recrystallisation from hot ether containing a little aniline. It melts at 127—128°, decomposes at a higher temperature, and is insoluble in benzene, and almost insoluble in cold ether and chloroform, but more readily in hot xylene, and readily in aniline; it is quickly decomposed by warm water and by cold alkalis.

Arsenanilidodibromide, $AsBr_2 \cdot NHPh$, prepared from arsenic tribromide, as described in the case of the corresponding dichloride, separates from ether in small, yellow crystals, melts at 111—113°, and decomposes at a higher temperature; it is more sparingly soluble in ether and chloroform, and more sensitive to moisture than the dichloride.

Arsenanilidodimethoxide, $NHPh \cdot As(OMe)_2$, is formed when the dibromide is boiled with an ethereal solution of the theoretical quantity of sodium methoxide; it is a colourless, highly refractive liquid, which boils at 55° under a pressure of about 12 mm., and at 159—162° under the ordinary atmospheric pressure with slight decomposition; it turns yellow on keeping.

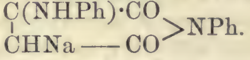
Arsenanilidodiethoxide, $NHPh \cdot As(OEt)_2$, prepared in like manner, boils at 78° under a pressure of about 12 mm., and at 178—181° under the ordinary atmospheric pressure with slight decomposition. The two compounds just described are very readily decomposed by water, yielding arsenious oxide, aniline, and the corresponding alcohol.

Arsendianilidobromide, $AsBr(NHPh)_2$, can be prepared as described in the case of the corresponding chloride; it separates from hot ether containing a little aniline in well-defined, transparent, seemingly rhombic crystals, which soon turn red and become cloudy on exposure to the air; it decomposes at 170—180°, is insoluble in benzene, and only sparingly soluble in ether and chloroform, and is quickly decomposed by water and alkalis.

The compound of the composition $As(NHPh)_3,3HCl$, described by Schiff (*Compt. rend.*, **56**, 1095) and by Leeds (*Amer. Chem. J.*, **3**, 134), could not be obtained; it is most probably a mixture of arsenanilidodichloride, arsendianilidochloride, and aniline hydrochloride. Landau (*Inaug. Diss. Berlin*, 1888) has described two compounds of the composition $AsCl_3,4C_6H_5{\cdot}NH_2 + H_2O$ and $AsBr_3,3C_6H_5{\cdot}NH_2 + H_2O$, which he obtained by treating aniline with arsenic trichloride and arsenic tribromide respectively in benzene solution; the authors find that Landau's bromo-compound is simply aniline hydrobromide, so that his results are not trustworthy. F. S. K.

Combination of Ethyl Oxalate with Anilides. By W. WISLICENUS and W. SATTLER (*Ber.*, **24**, 1245—1256).—By the action of sodium ethoxide on a mixture of ethyl oxalate and acetanilide in benzene solution, these two compounds unite in a manner similar to ethyl oxalate and ethyl acetate (Abstr., 1888, 1178), forming *ethyl sodoxalacetanilate*, $COOEt{\cdot}CO{\cdot}CHNa{\cdot}CO{\cdot}NHPh$. This separates out from the benzene solution, and is purified by recrystallisation from hot alcohol. It forms stellate groups of small plates, which slowly dissolve in cold, and are decomposed by hot, water. When heated to boiling with water, acidified, and quickly cooled, it yields *ethyl oxalacetanilate*, $COOEt{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHPh$, as an oil which quickly solidifies, and may then be recrystallised from light petroleum. It is very readily soluble in alcohol, ether, benzene, and alkalis, sparingly in light petroleum, and insoluble in water, melts at 87—88°, and decomposes at 130°. Its alcoholic solution is coloured red by ferric chloride.

The above sodium compound is not formed in very large quantities in the reaction, several other products being obtained; one of these is a sodium compound of the formula $C_{10}H_6NO_3Na$, which is exceedingly difficult to purify, and possibly consists of *sodium oxalacetophenylimide*,

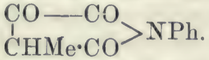


$$\begin{matrix} C(NHPh){\cdot}CO \\ | \\ CHNa \text{ --- } CO \end{matrix}{>}NPh$$

By the action of acids, it quickly undergoes alteration, forming complicated products, one of which is anilidomaleïc phenylimide (Abstr., 1890, 379); the chief product, however, is a yellow compound of unknown composition and constitution, termed by the authors *xanthoxalanil*, which is also the chief constituent of the original product of the reaction of sodium ethoxide on ethyl oxalate and acetanilide. It is best prepared from the latter by adding water, shaking well, acidifying, and warming the aqueous solution. The yellow, crystalline product obtained is boiled with acetic acid, which removes anilidomaleïc phenylimide. Xanthoxalanil remains as a yellow, crystalline product which is insoluble in the ordinary solvents, and decomposes, on heating with alkalis, into aniline, oxalic acid, and volatile organic acids.

Sodium ethoxide acts on a mixture of ethyl oxalate and acetoparatoluidide in a similar manner. The sodium compound formed could not be recrystallised, and was therefore at once acidified and cooled. *Ethyl oxalacetoparatoluidate*, $COOEt\cdot CO\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4Me$, is thus obtained as an oil which quickly solidifies, and on recrystallisation from benzene forms yellowish plates, melts at 134—135°, and is readily soluble in alcohol and ether. In this case also the chief product of the reaction is a yellow, insoluble compound, for which the name *xanthoxalotoluidil* is proposed. It forms microscopic plates and melts at 259°.

When a mixture of ethyl acetanilide and ethyl oxalate is heated with sodium ethoxide, the reaction proceeds in a normal manner, without the formation of condensation products. No sodium compound could be isolated, but the chief portion of the ethyl oxalethylacetanilate was found in the ethereal solution. It is purified by conversion into the *copper* salt, $(C_{14}H_{16}NO_4)_2Cu$, which crystallises from alcohol in slender, pale-green needles, and melts at 137—139°. The free *ethyl oxalethylacetanilate*, $COOEt\cdot CO\cdot CH_2\cdot CO\cdot NEtPh$, is obtained from it by acidifying and extracting with ether, and crystallises from the latter in large, lustrous, oblique prisms melting at 67—69°. It decomposes at 160°, and is soluble in the usual solvents with the exception of water and dilute soda, the alcoholic solution giving a dark-red coloration with ferric chloride.

When propionanilide is substituted for ethylacetanilide in the above reaction, the corresponding ethyl oxalpropionanilate is not obtained, but a compound containing the elements of alcohol less, which is probably *methyloxalacetophenylimide*,  $\left.\begin{array}{l}\mathrm{CO{-}{-}CO}\\ \quad|\\ \mathrm{CHMe\cdot CO}\end{array}\right>\mathrm{NPh}$. It may be recrystallised from benzene, and then melts at 191—192°, becoming yellow at the same time; it is readily soluble in alcohol, ether, and benzene, sparingly in water and light petroleum, and gives with ferric chloride in alcoholic solution a dirty, brownish-red coloration.

H. G. C.

Action of Alkalis and Amines on Halogen-substituted Quinones. By F. KEHRMANN (*J. pr. Chem.* [2], **43**, 260—267).—In his previous paper (Abstr., 1890, 136), the author stated that, by reduction with stannous chloride under certain conditions, the β-series of the halogen-substituted quinones yield the α- as well as the β-series of corresponding quinols. This is a mistake; experiments upon carefully purified β-dimethoxydichloroquinone show that the α-quinol cannot be obtained from it by reduction.

Chlorethoxydianilidoquinone, $C_{20}H_{17}N_2ClO_3$, is obtained by dissolving the crude mixture of α- and β-diethoxydichloroquinones (*loc. cit.*) in alcohol, adding aniline equal in weight to that of the mixed quinones, and leaving the mixture for half an hour in the cold; the precipitated chloranilanilide is then filtered off, and more aniline added to the filtrate, which is then boiled for a quarter of an hour; the liquid is filtered while hot, the precipitate washed with hot benzene, and the mixed filtrate and washings evaporated to crystallisation. Chlorethoxydianilidoquinone crystallises in long, steel-blue needles, melts at 232—233°, and partially sublimes undecomposed; it is insoluble in water and aqueous potash, which shows the absence of the hydroxyl group; it dissolves in alcoholic potash with an intense, brownish-red colour, and in concentrated sulphuric acid with a violet colour, like other dianilidoquinones and unlike anilidoquinols, which dissolve with an emerald-green colour, boiling alcohol, glacial acetic acid, and benzene dissolve it slightly, with an olive-green colour.

When aniline acts on α-diethoxydichloroquinone, both ethoxy-groups are eliminated (*loc. cit.*) from their para-positions, while the chlorine atoms remain. In the β-compound, one ethoxy-group and one chlorine atom are removed; hence neither the ethoxy-groups nor the chlorine atoms in the β-compound are in the para-positions; whether they are in the ortho- or meta-positions remains undecided. The constitution of chlorethoxydianilidoquinone is

$$[O_2 : OEt : Cl : (NHPh)_2 = 1 : 4 : 2 : 5 : 3 : 6].$$

Tetramethyldiamidochlorethoxyquinone, $[O_2 : (NMe_2)_2 : OEt : Cl = 1 : 4 : 2 : 5 : 3 : 6]$, is prepared by heating an alcoholic solution of β-diethoxydichloroquinone with a slight excess of dimethylamine, adding much water, and recrystallising the precipitate from dilute alcohol. It forms long, dark brownish-green needles, melts at 90—91°, is insoluble in cold, but slightly soluble in hot, water, and very soluble in alcohol, glacial acetic acid, ether, and benzene. *Dimethyldiamidochlorethoxyquinone*,

$$[O_2 : (NHMe)_2 : OEt : Cl = 1 : 4 : 2 : 5 : 3 : 6],$$

is formed when methylamine is substituted for dimethylamine; it crystallises in brownish-green leaflets melting with decomposition at 210°, and dissolves sparingly in boiling alcohol, but not at all in water. *Diamidochlorethoxyquinone*, formed when alcoholic ammonia is used, crystallises in long, dark-violet needles.

Chlorethoxyparadihydroxyquinone,

$$[O_2 : (OH)_2 : OEt : Cl = 1 : 4 : 2 : 5 : 3 : 6],$$

is obtained by boiling a weak aqueous alcoholic solution of β-diethoxydichloroquinone with excess of potash for some minutes, adding hydrochloric acid, and shaking with ether; it forms chocolate-brown, leafy crystals, melts at 168—170°, and partially sublimes in slender needles; it is very soluble in alcohol, ether, and hot benzene, with a brownish-red colour, slightly soluble in cold water and cold benzene, insoluble in strong hydrochloric acid, and soluble in alkalis with a blue-violet colour. When hydrochloric acid is added to a strong solution of it in an alkali, it crystallises gradually in thick, lustrous, dark-brown, rhombohedric tables (with 1 mol. H_2O). Several metallic compounds of this quinone were obtained. *Anilidohydroxychlorethoxyquinone*, $[O_2 : OH : NHPh : OEt : Cl = 1 : 4 : 5 : 3 : 6]$, is obtained by evaporating an alcoholic solution of the quinone with aniline, adding water, acidifying with hydrochloric acid, collecting the precipitate and treating it with dilute ammonia to dissolve the anilide and leave the dianilide; on adding dilute sulphuric acid to the ammoniacal liquid, the anilide is precipitated in steel-blue needles. It melts with complete decomposition at about 180°, and dissolves easily in alcohol and glacial acetic acid with an ultramarine-blue colour.

The alkyl chloranilates are shown to be quinone derivatives, in that they form molecular compounds with the corresponding hydrochloranilates. *Tetrachlorotetramethoxyquinhydrone* crystallises in brilliant, ruby-red tables and prisms with a faint-green, metallic lustre, when dimethyl chloranilate and dimethyl hydrochloranilate, in molecular proportion, are dissolved in a boiling mixture of equal volumes of alcohol and glacial acetic acid. *Tetrachlorotetrethoxyquinonehydrone*, similarly obtained, forms long, dark blood-red needles. A. G. B.

Symmetrical Trinitrosophenylparabromazobenzene. By C. Willgerodt (*Ber.*, **24**, 1320).—*Trinitrosophenylparabromazobenzene*, $C_6H_2(NO)_3{\cdot}N_2{\cdot}C_6H_4Br$ [$N:(NO)_3 = 1:2:4:6$; $N:Br = 1:4$], is prepared by the reduction of picrylparabromophenylhydrazine, trinitrophenylparabromazobenzene, dinitronitrosophenylparabromazobenzene, or nitrodinitrosophenylparabromazobenzene with potassium iodide in acetic acid solution; the compound crystallises from glacial acetic acid in yellow needles melting at 215°; it is soluble in alcohol, benzene, or chloroform, but dissolves very sparingly in ether, and is insoluble in water. J. B. T.

Picrylchlorophenylhydrazine and Related Compounds. By C. Willgerodt and A. Böhm (*J. pr. Chem.* [2], **43**, 482—496).—*Picrylparachlorophenylhydrazine*, $C_6H_2(NO_2)_3{\cdot}NH{\cdot}NH{\cdot}C_6H_4Cl$, exists in two distinct modifications. A red, stable variety is obtained by warming together molecular proportions of 4-chlorophenylhydrazine and picryl chloride, in alcoholic solution. It crystallises from organic solvents in well-formed prisms, and decomposes at 174—175°. The other variety is formed by dissolving the chlorophenylhydrazine and picryl chloride in cold chloroform, and shaking the mixed solutions in the cold, when the compound separates as an amorphous, yellow mass. On recrystallisation from cold chloroform, slender, yellow needles which decompose at 170—171° are obtained. The yellow modification is rapidly converted into the red modification when boiled for a short time with alcohol, ether, or water.

Picrylparachlorazobenzene, $C_6H_2(NO_2)_3{\cdot}N_2{\cdot}C_6H_4Cl$, is obtained by the oxidation of picrylparachlorophenylhydrazine with an alcoholic solution of iodine or a solution of chromic acid in acetic acid. It crystallises from alcohol in reddish-yellow needles, and melts at 138—139°.

Dinitronitrosophenylparachlorazobenzene, $NO{\cdot}C_6H_2(NO_2)_2{\cdot}N_2{\cdot}C_4H_4Cl$.—This compound is obtained when picrylparachlorophenylhydrazine is boiled in a reflux apparatus with glacial acetic acid, until the red colour at first formed is changed to a bright yellow. On cooling the solution, soft, slender, yellow needles separate; these dissolve in acetic acid, benzene, and alcohol, and melt at 242—243°.

Dinitronitrosoparachlorazoxybenzene, $NO{\cdot}C_6H_2(NO_2)_2{\cdot}N_2O{\cdot}C_6H_4Cl$, results on further oxidation of the corresponding azo-compound with a mixture of chromic and acetic acids. It crystallises from acetic acid in yellow needles, melts at 223—224°, and is readily soluble in benzene and chloroform.

Dinitrosonitrophenylparachlorazobenzene, $NO_2\cdot C_6H_2(NO)_2\cdot N_2\cdot C_6H_4Cl$, crystallises in greyish-yellow needles, and melts at 200°. It is obtained by heating picrylparachlorophenylhydrazine with alcohol for two hours at 110—120°.

Picrylnitroparachlorazobenzene, $C_6H_2(NO_2)_3\cdot N_2\cdot C_6H_3Cl\cdot NO_2$. This compound is prepared by boiling picrylparachlorazobenzene with three times its weight of a mixture of nitric and sulphuric acids for 3—4 hours. It crystallises best from alcohol in reddish-yellow scales, and melts with decomposition at 184—185°.

Dinitronitrosophenylparachlorazobenzene,

$$NO\cdot C_6H_2(NO_2)_2\cdot N_2\cdot C_6H_3Cl\cdot NO_2,$$

obtained on nitration of dinitronitrosophenylparachlorazobenzene with a mixture of nitric and sulphuric acids, crystallises from benzene or acetic acid in slender, yellow needles, and melts with decomposition at 180—181°. When this compound is heated for several hours with a very large excess of fuming nitric acid (sp. gr. 1·5) in presence of concentrated sulphuric acid, *dinitronitrosophenyldinitroparachlorazobenzene*, $NO\cdot C_6H_2(NO_2)_2\cdot N_2\cdot C_6H_2Cl\cdot NO_2$, is formed, which crystallises in whitish-yellow needles, and decomposes at 160—161°, some 20° lower than the compound containing one nitro-group less. On continued boiling with a mixture of the acids, further nitration does not take place.

2 : 4-*Dinitrophenylparachlorophenylhydrazine* is formed on heating together, in alcoholic solution, α-dinitrochlorobenzene (1 mol.) and parachlorophenylhydrazine. It crystallises from alcohol or benzene in beautiful, blood-red prisms, decomposes at 148—149°; and, on oxidation with chromic acid in acetic acid, forms the corresponding *dinitrophenylparachlorazobenzene*, $C_6H_3(NO_2)_2\cdot N_2\cdot C_6H_4Cl$, which is dissolved by organic solvents, crystallises in reddish needles, and melts at 151—152°.

Nitronitrosophenylparachlorazobenzene, $NO\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_4Cl$, is obtained on heating a mixture of 2 : 4-dinitrophenylparachlorophenylhydrazine and acetic acid in a reflux apparatus for ½ to 1 hour. It crystallises from acetic acid in beautiful, greenish-yellow needles, and melts at 217—218°.

2 : 4-*Dinitrosophenylparachlorazobenzene*, $C_6H_3(NO)_2\cdot N_2\cdot C_6H_4Cl$, is formed when the corresponding dinitrophenylparachlorophenylhydrazine is reduced by boiling it with alcohol; or more rapidly by heating together the two substances in a sealed tube at 115—120° for 2—3 hours. On evaporation of its alcoholic solution, dark-red crystals are deposited, which decompose at 126—127°.

2 : 4-*Dinitrophenylnitroparachlorazobenzene*, obtained by heating for one hour a mixture of 2 : 4-dinitrophenylparachlorazobenzene with three times its weight of a mixture of nitric with sulphuric acid. It crystallises from acetic acid in yellow needles, and melts at 122—123°.

Trinitronitrosoazobenzenephenylhydrazine,

$$N_2H_2Ph\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_2(NO_2)_2\cdot NO,$$

is prepared by heating together in a reflux apparatus phenylhydrazine (2 mols.) and trinitronitrosoparachlorazobenzene (1 mol.). It crystallises in dark-brown, microscopic scales which decompose at 115—116°.

Tetranitroazobenzeneparachlorophenylhydrazine,

$$C_6H_4Cl\cdot N_2H_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_2(NO_2)_3,$$

obtained in a similar way to the last-described compound, crystallises in imperfect, dark-red, microscopic prisms, decomposes at 117—119°, and, on boiling 4—5 hours with acetic acid, gives *trinitronitrosoazobenzeneparachlorazobenzene*, $C_6H_4Cl\cdot N_2\cdot C_6H_3(NO)\cdot N_2\cdot C_6H_2(NO_2)_3$, which forms reddish-yellow crystals, and decomposes at 202—203°.

Trinitronitrosoazobenzeneparachlorophenylhydrazine,

$$C_6H_4Cl\cdot N_2H_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_2(NO_2)_2\cdot NO,$$

is formed by the action of trinitrosophenylparachlorazobenzene (1 mol.) on parachlorophenylhydrazine (2 mols.). It has a dark-red colour, and decomposes at 110—112°; on oxidation with chromic and acetic acids, it gives *trinitronitrosoazobenzeneparachlorazobenzene*, $C_6H_4Cl\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_2(NO_2)_2\cdot NO$, which crystallises in yellow needles, and decomposes at 217—218°; and on reduction by heating for 4—5 hours with alcohol in sealed tubes at 120°, furnishes *trinitrosonitroazobenzeneparachlorazobenzene*,

$$C_6H_4Cl\cdot N_2\cdot C_6H_3(NO)\cdot N_2\cdot C_6H_2\cdot (NO)_2\cdot NO_2,$$

which only crystallises imperfectly, and decomposes at 146—147°.

Trinitronitrosoazobenenenitroparachlorazobenzene,

$$NO_2\cdot C_6H_3Cl\cdot N_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_2(NO)_2\cdot NO_2,$$

is obtained when trinitronitrosoazobenzeneparachlorazobenzene is boiled for 2—3 hours with three times its weight each of nitric acid (sp. gr. 1·5) and concentrated sulphuric acid. It forms whitish-yellow crystals, only slightly soluble in alcohol, and decomposes at 189—190°.

Tetranitronitrosodisazobenzeneparachlorophenylhydrazine,

$$C_6H_4Cl\cdot N_2H_2\cdot C_6H_3(NO_2)\cdot N_2\cdot C_6H_4(NO_2)\cdot N_2\cdot C_6H_2(NO_2)_2\cdot NO.$$

This compound is obtained by adding parachlorophenylhydrazine (2 mols.) to trinitronitrosoazobenzenenitroparachlorazobenzene (1 mol.) suspended in alcohol. It forms an almost amorphous, dark-red product, and decomposes at 120—122°.

That the above-described nitroso-compounds are simple azo-compounds, and not polymerides, is shown by the fact that their molecular weights, as determined by Raoult's method, agree with those calculated from the above-given formulæ. G. T. M.

Amidotolyloxamethane. By H. Schiff and A. Vanni (*Ber.*, **24**, 1315—1317; compare this vol., p. 702).—*Toluylenedioxamethane*,

$C_6H_3Me(NH{\cdot}CO{\cdot}COOEt)_2$ [Me : NH : NH = 1 : 2 : 4], is prepared by heating amidotoluyloxamethane with ethyl oxalate and a little alcohol; it is also found in the mother liquors obtained in the preparation of amidotolyloxamethane from ethyl oxalate and toluylenediamine; the compound is sparingly soluble in ether, from which it crystallises in needles melting at 130°; the alcoholic solution is fluorescent.

Oxamethanetolyloxamide, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}CO{\cdot}COOEt$ [= 4 : 1 : 2], is formed from amidotolyloxamide and ethyl oxalate in a similar manner to the preceding compound; it crystallises from dilute alcohol in tufts of colourless needles, and melts at 210° with decomposition. By the action of alcoholic ammonia on either of the preceding compounds, *toluyldioxamide*, $C_6H_3Me(NH{\cdot}C_2O_2{\cdot}NH_2)_2$, is obtained as a white, crystalline powder decomposing above 220° without melting. *Toluylenedioxamic acid*, $C_6H_3Me(NH{\cdot}CO{\cdot}COOH)_2$, is found in the aqueous mother liquors of the dioxamide; it is an unstable, viscid liquid, excessively sweet to the taste; the *barium salt* crystallises with $1H_2O$, and, like the *silver* and *lead salts*, readily undergoes decomposition.

Uramidotolyloxamethane, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me{\cdot}NH{\cdot}CO{\cdot}COOEt$, is prepared by the action of potassium cyanate on amidotolyloxamethane sulphate in aqueous solution; it crystallises from alcohol, and melts at 218°. On treatment with ammonia, or by the action of potassium cyanate on amidotolyloxamide sulphate, *uramidotolyloxamide*, $C_6H_3Me(NH{\cdot}CO{\cdot}NH_2)_2$, is formed; this is sparingly soluble in alcohol, and melts at 239° with partial decomposition. J. B. T.

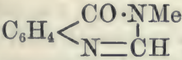
Ethyl Acetoacetate Aldehydeuramide. By P. Biginelli (*Ber.*, **24**, 1317—1312).—On boiling an alcoholic solution of ethyl acetoacetate, benzaldehyde, and carbamide in molecular proportion for two hours in a reflux apparatus, a compound is obtained crystallising in colourless, lustrous plates and melting at 207—208°; its constitution is expressed by one or other of the following formulæ, of which the second appears to be the more probable:—

$$CHPh{:}N{\cdot}CO{\cdot}N{:}CMe{\cdot}CH_2{\cdot}COOEt;\ CHPh{:}N{\cdot}CO{\cdot}NH{\cdot}CMe{:}CH{\cdot}COOEt.$$

The same substance is also formed by the interaction of ethyl uramidocrotonate and benzaldehyde. It is very stable, and is not affected by concentrated acids or alkalis in the cold; on boiling with dilute sulphuric acid, benzyl alcohol is produced, whilst, by heating with potash, it decomposes into benzyl alcohol, benzaldehyde, ammonia, and potassium carbonate; a yellow substance is also formed in small quantity, and is being further investigated. Salicylaldehyde, cinnamaldehyde, furfuraldehyde, cumaldehyde, and other aldehydes react in a manner similar to benzaldehyde, whilst the ethyl acetoacetate may be replaced by acetophenone or acetone; the resulting products are, however, less stable. J. B. T.

Formyl and Oxalyl Derivatives of Orthamidobenzamide. By E. Knape (*J. pr. Chem.* [2], **43**, 209—231).—The orthamidobenzamide employed in this work was prepared from isatoic acid, itself prepared from isatin as described by Kolbe (Abstr., 1885, 665). Concerning the preparation of isatin, the author remarks that oxidation of indigo by chromic acid yields a purer product, whilst oxidation by nitric acid yields a larger quantity; he gives directions for obtaining a yield of 30—35 per cent. of pure isatin by Sommargau's method with nitric acid (*Ber.*, **17**, 976). The orthamidobenzoic acid was prepared by reducing orthonitrobenzoic acid with tin and hydrochloric acid in alcohol; the yield was 47—50 per cent.

Formylorthamidobenzamide (Weddige, Abstr., 1885, 661) is best obtained by stirring orthamidobenzamide (1 mol.) with 95 per cent. formic acid ($1\frac{1}{2}$ mols.) until the mass is solid, evaporating the excess of acid on the water-bath, and crystallising from hot alcohol. It forms colourless, lustrous, rhombohedral crystals, sometimes needles; it dissolves in all hot solvents, and in most of them when cold; it melts at 123°, and when heated at 170°, or for some time with water or alkalis, it loses water and forms δ-oxyquinazoline (*loc. cit.*); this substance crystallises in long, slender, white needles, melts at 211—212°, and dissolves in the usual solvents, including acids and alkalis, except light petroleum; its solutions, especially the aqueous, fluoresce blue; its *platinochloride* forms an orange-red, microcrystalline precipitate.

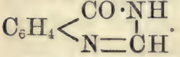
γ-Methyl-δ-oxyquinazoline,  $C_6H_4<\begin{array}{l}CO\cdot NMe\\ \quad\;\;|\\ N{=}CH\end{array}$, is obtained by dissolving δ-oxyquinazoline in the calculated quantity of a solution of potash in methyl alcohol, and adding the calculated quantity of methyl iodide; it crystallises in long, lustrous needles, melts at 71°, and dissolves in the usual solvents, but will not crystallise from light petroleum. The *platinochloride* is described.

When orthamidobenzamide and 95 per cent. formic acid are stirred together in molecular proportion, *formyldiorthamidobenzamide*, $OH\cdot CH(NH\cdot C_6H_4\cdot CONH_2)_2$, is obtained; it crystallises in thin, nearly quadratic, rhombic leaves or tables, melts at 135°, and dissolves freely in water, alcohol, benzene, ether, acetone, and hot chloroform; prolonged heating with water, alcohol, or dilute alkalis converts it into δ-oxyquinazoline; when heated at 150° until no more water is evolved, it yields a crystalline mass which gradually melts between 170° and 180°, and is so readily converted into δ-oxyquinazoline and orthamidobenzamide that it could not be analysed. Attempts to obtain a methyl derivative of formyldiorthamidobenzamide resulted in the formation of γ-methyl-δ-oxyquinazoline and orthamidobenzamide. The *platinochloride* forms long, slender, lustrous, yellowish-red needles, which dissolve in alcohol with a blue fluorescence. A *substance* melting at 107—108° was obtained during the preparation of formyldiorthamidobenzamide, but in quantity insufficient for analysis.

Formylorthamidobenzomethamide, $CHO\cdot NH\cdot C_6H_4\cdot CO\cdot NHMe$, is obtained by mixing orthamidobenzomethylamide (Abstr., 1887, 1043) with formic acid in molecular proportion, evaporating on the water-bath, and crystallising from benzene; it forms clusters of needles, melts at 111—112° and dissolves in warm ether and benzene, less easily in water and alcohol, and not at all in light petroleum; when heated at 190—200° for some hours, it is converted into γ-methyl-δ-oxyquinazoline. The *methiodide*, $C_{10}H_{11}N_2OI$, is obtained by heating formylorthamidobenzomethylamide with the calculated quantity of methyl iodide in methyl alcohol at 100° in a sealed tube for one hour; it crystallises in needles and leaflets; its *platinochloride*, for obtaining which it is converted into chloride by double decomposition with silver chloride, is an orange-yellow, crystalline powder insoluble in alcohol and ether; the corresponding *hydroxide* forms very slender crystals which are very soluble in water.

Weddige (Abstr., 1887, 1044) treated orthamidobenzamide with methyl iodide in alcohol in order to obtain orthomethamidobenzamide; the author substituted methyl for ethyl alcohol, and obtained dimethamidobenzamide at the same time. Orthamidobenzamide is dissolved in methyl alcohol, and heated with the calculated quantity of methyl iodide in a sealed tube at 100° for some hours; the mass is extracted with ether, the residue dissolved in as little water as possible, the solution filtered, the bases precipitated by ammonia, washed with cold water, and then treated with water at 70—80°; dimethamidobenzamide and unaltered orthamidobenzamide are thus dissolved, and on cooling, the former crystallises out. *Dimethamidobenzamide*, $NMe_2\cdot C_6H_4\cdot CONH_2$, forms needles, melts at 139—140°, and dissolves easily in acids; its *platinochloride* was obtained.

Formylorthomethamidobenzamide, $CHO\cdot NMe\cdot C_6H_4\cdot CONH_2$, is prepared by heating orthomethamidobenzamide with the calculated quantity of formic acid in a tube at 100° for three hours; after decolorising with animal charcoal in alcohol, it crystallises in feathery, flat needles which soften about 100° and melt at 113°. When heated at 150—160° for some time, it yields a thick, yellow oil which solidifies after some days to small needles melting at 123—124°; the quantity obtained was insufficient to allow of this substance being identified as α-methyl-δ-oxyquinazoline, but it is certainly distinct from γ-methyl-δ-oxyquinazoline. The identity of the methyl derivatives obtained from formylorthamidobenzomethamide and from δ-oxyquinazoline proves that the constitution of the latter is



$$C_6H_4{<}\begin{matrix}CO\cdot NH\\ \quad | \\ N{=}CH\end{matrix}.$$

The author has prepared Griess' carbimidoamidobenzoyl (Abstr., 1885, 1227), and finds that it melts at 211—212°, not 214°; he therefore concludes that it is identical with δ-oxyquinazoline, and that Griess' formula for it is incorrect.

Ethyloxalylorthamidobenzamide, $COOEt\cdot CO\cdot NH\cdot C_6H_4\cdot CONH_2$, was obtained once in several experiments, when the calculated quantities of orthamidobenzamide and ethyl oxalate were gradually heated together to 170°, alcohol being evolved. An amorphous precipitate separated from the alcoholic solution of the product; this was a mixture of several substances, from which, by fractional crystallisation, small, prismatic crystals of this ethyl derivative, melting at 158—159°, were obtained. From the mother liquor, a substance, $C_{55}H_{58}NO_2$, was obtained in needles melting at 140—141°; the amount was insufficient for further investigation. A fibrous *substance* of uncertain composition melting at 177—178° was obtained when methyl oxalate was substituted for ethyl oxalate.

An *additive product* is obtained when orthamidobenzamide and ethyl oxalate are heated in alcohol; it forms thick, flat prisms, melts at 87—90°, and dissolves in cold alcohol, water, ether, acetone, and warm chloroform; it is decomposed into ethyl oxalate and orthamidobenzamide when heated at 80° for some time, or by the action of hydrochloric acid. A similar product is obtained with methyl oxalate; it forms short, slender needles, melts gradually between 80° and 90°, and dissolves in the usual solvents. A. G. B.

Alkyl Ketones from Halogen Derivatives of Aromatic Hydrocarbons. By A. Claus (*J. pr. Chem.* [2], **43**, 355—363; compare Schweitzer, this vol., p. 684).

Orthochlorometamethyltolyl methyl ketone (*orthochlorometacetyltoluene*) [Me : Cl : COMe = 1 : 2 : 5] is obtained by the action of acetic chloride on orthochlorotoluene in carbon bisulphide in the presence of aluminium chloride; it is a colourless, strongly refractive liquid of agreeable aromatic odour, boiling at 238—242° (uncorr.); its *oxime* crystallises in thick, yellowish needles and melts at 112° (uncorr.). By oxidation with potassium permanganate in alkaline solution, it yields parachlorometatoluic acid [COOH : Me : Cl = 1 : 3 : 4] (m. p. 209°, uncorr.; Abstr., 1885, 1052), whose *calcium* salt crystallises with 3½ mols. H_2O, and 4-chlorisophthalic acid [$(COOH)_2$: Cl = 1 : 3 : 4], which does not melt below 340°; this oxidation shows that in the ketone the acetyl group must occupy the para-position to the chlorine atom, and the meta-position to the methyl group.

Orthobromometamethyltolyl methyl ketone [Me : Br : COMe = 1 : 2 : 5] is prepared in like manner, and is a colourless, strongly refractive oil of agreeable, aromatic odour; it boils at 262—264° (uncorr.); its *oxime* crystallises in thick, white needles, and melts at 104° (uncorr.). When oxidised with permanganate, it yields parabromometatoluic acid (m. p. 209°, uncorr.; Abstr., 1882, 185), whose *barium* salt crystallises with 4 mols. H_2O, and 4-*bromisophthalic acid* (m. p. 287°, uncorr.), whose *barium* salt (with 1 mol. H_2O) is described.

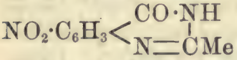
When parachlorotoluene and parabromotoluene are acetylised in this way, the products seem to be mixtures; in the former case, the product boils at 235—240° (uncorr.), in the latter, at 261—265°.

Metachlororthomethyltolyl methyl ketone [Me : COMe : Cl = 1 : 2 : 5], similarly obtained, is a colourless, agreeably aromatic liquid which boils at 239—240° (uncorr.); its *oxime* crystallises in long, colourless, lustrous needles melting at 116° (uncorr.). By oxidation with permanganate, it yields parachlororthotoluic acid (m. p. 166°, uncorr.) and parachlorophthalic acid (m. p. 148°).

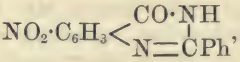
Metabromorthomethyltolyl methyl ketone is a colourless oil of agreeable aromatic odour which boils at 257—258° (uncorr.); its *oxime* forms long, soft, filamentous needles, and melts at 97° (uncorr.). By oxidation with permanganate it yields parabromorthotoluic acid (m. p. 187°, uncorr.) and parabromophthalic acid (m. p. 168°), whose anhydride melts at 106°.

4-*Chlorometaxylyl methyl ketone* is a colourless, aromatic oil, boiling at 260° (uncorr.); its oxime forms colourless needles, and melts at 103° (uncorr.). A. G. B.

Action of Ammonia on Derivatives of the Ethyl and Methyl Salts of Orthamidobenzoic Acid. By E. ZACHARIAS (*J. pr. Chem.* [2], **43**, 432—450; compare Hübner, *Annalen*, **195**, 34).—*Ethyl amidonitrobenzoate* [$COOEt : NH_2 : NO_2 = 1 : 2 : 3$] is obtained by heating in a sealed tube at 130—150° a mixture of ethyl nitroethoxybenzoate [$COOEt : OEt : NO_2 = 1 : 2 : 3$] and alcoholic ammonia. It crystallises from 90 per cent. alcohol in beautiful, dark-yellow needles, and melts at 109°. On continued digestion with baryta-water, and subsequent addition of hydrochloric acid to the sparingly soluble barium salt thus obtained, a substance identical with amidonitrobenzoic acid [$COOH : NH_2 : NO_2 = 1 : 2 : 3$] separates.

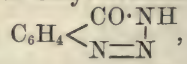
Ethyl acetamidonitrobenzoate [$COOEt : NHAc : NO_2 = 1 : 2 : 3$] is obtained by heating together a mixture of ethyl amidonitrobenzoate and acetic chloride. It crystallises from water in white needles, melts at 102°, and is exceedingly soluble in cold alcohol, ether, benzene, chloroform, and light petroleum. On digestion with aqueous ammonia, it forms the corresponding *ammonium salt*, but, on heating in a sealed tube at 170° with alcoholic ammonia, the compound  $NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ N{=}CMe\end{matrix}$ is obtained. This compound is insoluble in ordinary solvents, except hot alcohol, from which it separates in small, brownish crystals; it melts with decomposition at 264°, gives a potassium salt crystallising in yellowish-red needles, and a methyl salt crystallising in white needles which melt at 175°; it forms insoluble salts with the heavy metals; and, on reduction with tin and hydrochloric acid or stannous chloride, gives a base which crystallises in colourless needles, and melts at 230—232°. On acetylation of ethyl amidonitrobenzoate, a yellow compound is obtained, which appears to be an isomeride of the ethyl acetamidonitrobenzoate melting at 102°.

Ethyl nitrobenzoylamidobenzoate [$COOEt : NHBz : NO_2 = 1 : 2 : 3$] is obtained by warming ethyl amidonitrobenzoate (m. p. 109°) with benzoic chloride. It forms yellowish-white crystals, melts at 85·5°, and is readily soluble in alcohol, ether, benzene, and chloroform. On heating it with alcoholic ammonia, it yields the compound



$$NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ N{=}CPh\end{matrix},$$

which crystallises in slender, white needles, not melting at 250°, and forms a methyl salt crystallising from alcohol in slender, white needles which melt at 138°.

On treating ethyl diazobenzoate chloride, $COOEt\cdot C_6H_4\cdot N_2Cl$ [$COOEt : N : NCl = 1 : 2$], obtained from ethyl orthamidobenzoate, with cold aqueous ammonia, benzazimide,  $C_6H_4<\begin{matrix}CO\cdot NH\\ N{=}N\end{matrix}$, is formed; but the author has not succeeded in producing a similarly constituted closed-chain compound by the action of aqueous ammonia on ethyl methylnitrosoamidobenzoate [COOEt : N(NO)Me = 1 : 2]. When the last-named compound is heated at 140—150° with aqueous ammonia, a mixture of orthonitrosomethylamidobenzamide and *methylamidobenzoic acid*, $COOH{\cdot}C_6H_4{\cdot}NHMe$ [COOH : NHMe = 1 : 2], is obtained. The latter softens at 165°, melts at 170°, is soluble in all ordinary solvents, but does not form well-characterised salts.

G. T. M.

Diethylcarbobenzonic Acid. By R. ANSCHÜTZ and W. BERNS (*Annalen*, **261**, 298—309).—The acid first prepared by Limpricht and Schwanert (*Annalen*, **155**, 63), by the action of alcoholic potash on deoxybenzoïn, and named by Zagoumenny (this Journal, 1877, ii, 194) diethylcarbobenzonic acid, has the composition $C_{18}H_{18}O_2$, but its constitution has not yet been ascertained. It distils under greatly reduced pressure with slight decomposition, and is insoluble in ammonia and alkaline carbonates, but soluble in concentrated potash; it seems not to contain a carboxyl group, and it does not combine with hydroxylamine, phenylhydrazine, or acetic anhydride. When treated with hydrogen chloride in alcoholic solution, it is converted into a colourless, liquid, *diethyl* derivative, which boils at 207—209° (11 mm.) and has the composition $C_{20}H_{22}O_2$. It is not acted on by sodium amalgam, but when distilled over zinc-dust it yields stilbene, and when boiled with hydriodic acid and amorphous phosphorus it is converted into a colourless, crystalline compound melting at 132—134°, which the authors name *isodiethylcarbobenzonic acid;* this substance is probably identical with the compound obtained by Limpricht and Schwanert (*loc. cit.*) by heating diethylcarbobenzonic acid at 100° with hydrochloric acid.

When diethylcarbobenzonic acid is boiled with excess of nitric acid of sp. gr. 1·18 until oxidation is at an end, it is converted into a compound of the composition $C_{18}H_{16}O_3$, which melts at 120°. On fusing it with potash in the manner described by Zagoumenny, an inflammable gas is evolved, and on dissolving the melt in water and acidifying with hydrochloric acid, there is produced a precipitate which is completely soluble in ammonia: when this product is distilled under greatly reduced pressure (12 mm.), it yields a small quantity of a colourless liquid with an odour of butyric acid, benzoic acid, and a thick, colourless oil boiling at about 176·5° (15 mm.), which has the composition $C_{11}H_{14}O_2$. On treating this oil with potassium permanganate, it is converted into benzoic acid; it is, therefore, a phenylvaleric acid, and not diethylbenzoic acid as was supposed by Zagoumenny; it is not identical with either of the known phenylvaleric acids, both of which, namely, the normal acid and phenylethylpropionic acid (benzylethylacetic acid), have been prepared by Baeyer and Jackson.

Ethyl phenylvalerate, $C_{13}H_{18}O_3$, prepared by treating the acid obtained from diethylcarbobenzonic acid with hydrogen chloride in alcoholic solution, is a colourless liquid boiling at 144—146° under a pressure of about 15 mm. The *chloride*, $C_{11}H_{13}OCl$, is obtained when the acid is treated with phosphorus pentachloride; it is a colourless liquid boiling at 129—131° under a pressure of about 11 mm. The *anilide*,

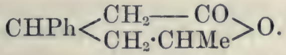
$C_{17}H_{19}NO$, prepared from the chloride, separates from alcohol in rhombic crystals, $a : b : c = 0{\cdot}68451 : 1 : 0{\cdot}60844$, melting at 101—102°.

Benzylethylacetic acid (phenylethylpropionic acid) can be prepared by hydrolysing ethyl benzylethylacetoacetate; it boils at 172—174° under a pressure of about 15 mm. The *chloride* is a colourless liquid boiling at 145—150° under a pressure of about 24 mm. The *anilide*, $C_{17}H_{19}NO$, separates from alcohol in large, well-defined, monosymmetric crystals, $a : b : c : = 0{\cdot}81716 : 1 : 1{\cdot}1885$, $\beta = 70° 28'$, melting at 88—89°. F. S. K.

Additive Products of Ethyl Sodacetoacetate and Sodiomalonate with Ethereal Salts of Unsaturated Acids. By A. Michael and P. C. Freer (*J. pr. Chem.* [2], **43**, 390—395; compare Auwers, this vol., p. 546).—The first product of the reaction of ethyl sodacetoacetate on ethyl cinnamate (Abstr., 1887, 672) is an additive compound of one molecule of the latter with two molecules of the former. The compound $C_{15}H_{16}O_4$ is obtained when this additive product is heated with alcohol; it melts at 144—145°, not 140·5° (*loc. cit.*), and gives an amorphous, white *hydrazone*, $C_{15}H_{16}O_3{:}N{\cdot}NHPh$, which melts at 74—75°. When the compound $C_{15}H_{16}O_4$ is saponified with alcoholic potash, a *potassium* salt is obtained; the corresponding *acid* melts at 95° with evolution of carbonic anhydride, yielding a compound $C_{12}H_{12}O_2$, which crystallises in long, lustrous needles, melts at 184—185°, and dissolves in alcohol and ether, but not in light petroleum.

The substance $C_{12}H_{12}O_2$ yields two *oximes*, the one, $C_{24}H_{22}O_3{:}NOH$, when a neutral (*sic*) solution of the substance in ammonia is mixed with hydroxylamine hydrochloride, as a white, amorphous precipitate which melts with decomposition at 129—131°; the other, $C_{12}H_{12}O{:}NOH$, when hydroxylamine is added to an aqueous or alcoholic solution of the substance, as a white, amorphous compound melting at 172° and soluble in alcohol and ether but not in light petroleum; it is thus proved that $C_{12}H_{12}O_2$ contains a carbonyl group. The compound $C_{24}H_{22}O_2{:}NPh$, obtained by heating $C_{12}H_{12}O_2$ with aniline (equal mols.) in alcohol, crystallises in white octahedra, melts at 237—238°, and is insoluble in aqueous sodium carbonate and hydroxide.

When the compound $C_{12}H_{12}O_2$ is heated for some time with aqueous alkalis, a new substance $C_{12}H_{14}O_3$ is obtained; it crystallises from light petroleum in concentric groups of needles, from water and carbon bisulphide in large, hard prisms, melting at 83—84°; it behaves as an acid but not an unsaturated one; with iodine in an alkaline solution, it yields iodoform; its *silver salt* (with ½ mol. H_2O) forms a white precipitate; its *oxime* is an amorphous substance, melts at 93°—94° with decomposition, and dissolves in alcohol and ether. Dilute potassium permanganate solution oxidises the substance $C_{12}H_{14}O_3$, with formation of benzoic acid and an unidentified, volatile acid. When reduced with sodium amalgam in alcohol, $C_{12}H_{14}O_3$ yields a thick oil, $C_{12}H_{14}O_2$, which distils undecomposed at 271—273° (17 mm.) and behaves as a lactone, thus indicating that $C_{12}H_{14}O_3$ is a carboxy-acid of the constitution $COMe{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}COOH$, the lactone being a δ-lactone of the constitution



$$CHPh<\begin{matrix}CH_2\text{—}CO\\CH_2\cdot CHMe\end{matrix}>O.$$

The substance $C_{12}H_{12}O_2$ has the same empirical formula as cinnamylacetone (m. p. 84°), but is not identical with it. A. G. B.

Derivatives of Phenyl Salicylate (Salol). By W. Knebel (*J. pr. Chem.* [2], **43**, 378—389; compare Abstr., 1890, 1284).—*Phenyl acetylsalicylate* (*acetylsalol*), $OAc\cdot C_6H_4\cdot COOPh$, is obtained by heating acetic chloride or acetic anhydride with dry phenyl salicylate and pouring the liquid into absolute alcohol; it forms stellate crystals and melts at 97°.

α-Phenyl nitrosalicylate [$NO_2 : OH : COOPh = 5 : 2 : 1$] has been already described (Abstr., 1890, 1284); it is also obtained by heating 5-nitrosalicylic acid (m. p. 222°; compare Hübner, Abstr., 1879, 380) with phenol and phosphorus oxychloride at 120—130° for several hours (compare Nencki and Rasinsky, *J. pr. Chem.* [2], **31**, 472).

β-Phenyl nitrosalicylate [$NO_2 : OH : COOPh = 3 : 2 : 1$] is prepared by heating 3-nitrosalicylic acid with phenol and phosphorus oxychloride at 100°; it crystallises in prisms which melt at 101°.

α-Phenyl acetylnitrosalicylate, prepared from α-phenyl nitrosalicylate and acetic anhydride, crystallises in slender, white needles melting at 118°. The nitration of phenyl acetylsalicylate with nitric acid only yields α-phenyl nitrosalicylate. *β-Phenyl nitracetylsalicylate*, prepared from β-phenyl nitrosalicylate and acetic anhydride, melts at 95°.

Phenyl dinitrosalicylate (Abstr., 1890, 1284), is sparingly soluble in alcohol, more so in benzene and chloroform, and most so in glacial acetic acid. *Phenyl dinitracetylsalicylate* crystallises in slender, white needles and melts at 118°.

Orthonitrophenyl dinitrosalicylate (phenyl trinitrosalicylate, *loc. cit.*) is obtained by acting on phenyl salicylate with a mixture of nitric acid (sp. gr. 1·525) and strong sulphuric acid; it crystallises in silvery leaflets and melts at 100°. By saponification it yields orthonitrophenol. *Paranitrophenyl dinitrosalicylate* is similarly obtained, but the reaction mass is extracted with glacial acetic acid instead of alcohol; it forms yellowish needles and melts at 176°; it yields paranitrophenol on hydrolysis. *Paranitrophenyl dinitracetylsalicylate* melts at 156°.

The author's attempts to obtain a trinitrosalicylic acid failed. An isomeride of dinitrosalicylic acid was obtained; it melts at 95° and is converted into the known acid (m. p. 173°) when recrystallised.

A. G. B.

Action of Ammonia and Methylamine on Derivatives of the Ethyl and Methyl Salts of Nitrohydroxybenzoic Acids. By P. Thieme (*J. pr. Chem.* [2], **43**, 451—482).—When a mixture of ethyl nitrohydroxybenzoate [$COOEt : NO_2 : OH = 1 : 3 : 4$] and alcoholic ammonia is heated together for 8—16 hours, at 180°, in sealed tubes, the compound $COOEt\cdot C_6H_3(NO_2)\cdot ONH_4$ is formed, without the least trace of a nitrohydroxybenzamide.

Ethyl nitrethoxybenzoate [$COOEt : NO_2 : OEt = 1 : 3 : 4$] crystallises from alcohol in nearly colourless needles or scales, melts at 64°, is insoluble in water, but dissolves readily in alcohol, ether, benzene, and chloroform. On digestion with alcoholic ammonia at 130—140°, it is converted almost quantitatively into *ethyl nitramidobenzoate* [$COOEt : NO_2 : NH_2 = 1 : 5 : 4$], which crystallises from alcohol in long, yellow needles, melts at 136°, and readily sublimes. If aqueous ammonia is employed instead of alcoholic ammonia, *ammonium nitramidobenzoate* is formed.

Nitramidobenzamide [$CONH_2 : NO_2 : NH_2 = 1 : 3 : 4$] is obtained when the above-described ethyl nitramidobenzoate (m. p. 136°) is heated with aqueous ammonia. It crystallises from water in long, felted, yellow needles, melts with decomposition at 226°, and sublimes at a lower temperature.

Ethyl nitracetamidobenzoate [$COOEt : NO_2 : NHAc = 1 : 3 : 4$] crystallises in long, white, felted needles, melts at 95—96°, readily sublimes, and is converted on heating with aqueous ammonia into *ammonium nitramidobenzoate.*

Ethyl nitromethamidobenzoate [$COOEt : NO_2 : NHMe = 1 : 3 : 4$] is readily formed by heating ethyl nitrethoxybenzoate (m. p. 64°) with methylamine (2 mols.) in alcoholic solution. It crystallises from alcohol in orange-yellow, prismatic masses, melts at 100°, and, on treatment with potash and subsequent addition of hydrochloric acid, gives a corresponding *nitromethamidobenzoic acid*, which crystallises from alcohol in pale-yellow needles, and melts with decomposition at 295°.

Ethyl dinitrohydroxybenzoate [$COOEt : (NO_2)_2 : OH = 1 : 3 : 5 : 4$] is obtained on further nitration of the mononitro-compound (m. p. 64°) with a mixture of nitric and sulphuric acids. It crystallises from alcohol in long, stout, yellow needles (compare Salkowsky, *Annalen*, **163**, 50), melts at 87°, and is converted by aqueous ammonia into the corresponding ammonium salt. *Ethyl dinitrethoxybenzoate* [$COOEt : (NO_2)_2 : OEt = 1 : 3 : 5 : 4$] crystallises in colourless needles melts at 56°, and is converted by alcoholic ammonia into the corresponding ethyl dinitramidobenzoate, which crystallises from alcohol in lemon-yellow, glistening scales, and melts at 114° (Salkowsky, *loc. cit.*).

Ethyl nitrethoxybenzoate [$COOEt : NO_2 : OEt = 1 : 4 : 5$] crystallises in white, prismatic needles, melts at 60—61°, and is converted, on heating at 180° with alcoholic ammonia, into the corresponding *nitrethoxybenzamide*, which crystallises from hot water in slender needles melting at 202°, and on hydrolysis with potash, and subsequent treatment with hydrochloric acid, gives the corresponding free *acid*, crystallising from alcohol in light-yellow needles, and melting at 216·5°. When heated with aqueous ammonia, ethyl nitrethoxybenzoate (m. p. 60—61°) is converted into *nitramidobenzoic acid* [$COOH : NO_2 : NH_2 = 1 : 4 : 5$], which crystallises from water in brick-red scales, and melts with decomposition at 290°.

Ethyl nitramidobenzoate [$COOEt : NO_2 : NH_2 = 1 : 4 : 5$] melts at 139° (compare Kayser, Abstr., 1886, 149), and is converted by alcoholic ammonia, at 160—170°, into *nitramidobenzamide*

$$[CONH_2 : NO_2 : NH_2 = 1 : 4 : 5],$$

which crystallises from water in slender, reddish-yellow needles, and melts at 231—232°.

Ethyl nitrethoxybenzoate [$COOEt : NO_2 : OEt = 1 : 4 : 5$] is converted, by heating with methylamine, into *nitromethamidobenzomethylamide* [$CONHMe : NO_2 : NHMe = 1 : 4 : 5$], which melts at 194°, and, on hydrolysis and subsequent treatment with acid, gives *nitromethylamidobenzoic acid* [$COOH : NO_2 : NHMe = 1 : 4 : 5$], crystallising from alcohol in rhombic plates or prisms, and melting with decomposition at 268°.

Nitrohydroxybenzoic acid [$COOH : NO_2 : OH = 1 : 2 : 3$] crystallises in yellow prisms containing 1 mol. H_2O, and, when anhydrous, melts at 178°. Its ethyl salt melts at 124°, and does not give a nitrohydroxybenzamide when heated with aqueous or alcoholic ammonia. The corresponding ethoxyethyl salt crystallises from alcohol in almost colourless, prismatic prisms or plates, melts at 53—54°, is not acted on by alcoholic ammonia, and gives, with aqueous ammonia, the original nitrohydroxybenzoic acid (m. p. 178°).

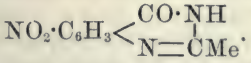
Ethyl nitrohydroxybenzoate [$COOEt : NO_2 : OH = 1 : 5 : 2$], which melts at 96°, gives Hübner's nitrohydroxybenzamide (m. p. 225°) on digestion with alcoholic ammonia. Under like conditions, the corresponding ethyl nitrethoxybenzoate (m. p. 68°) gives an ethyl nitramidobenzoate, which crystallises in slender, yellow needles melting at 145°, and corresponds in constitution with Hübner's nitroamidobenzoic acid (m. p. 263°).

Ethyl nitromethamidobenzoate [$COOEt : NHMe : NO_2 = 1 : 2 : 5$] is formed when the corresponding ethyl nitroethoxybenzoate (m. p. 194°) is heated in a sealed tube, at 150°, with methylamine (2 mols.). It crystallises in greenish-yellow needles, melts at 103°, and may be readily sublimed. The free acid crystallises in small, bright-yellow, pearly, rhombic plates, melts at 259°, and is easily soluble in alcohol and ether. *Nitromethamidobenzomethylamide*

$$[CONHMe : NHMe : NO_2 = 1 : 2 : 5]$$

crystallises in long, thin, yellow needles, melts at 204°, and readily sublimes.

Ethyl nitracetamidobenzoate [$COOEt : NHAc : NO_2 = 1 : 2 : 5$] forms long, colourless needles, melts at 153°, and is converted by alcoholic ammonia into *metanitro-β-methyl-δ-oxyquinazoline*,



$$NO_2\cdot C_6H_3{<}\begin{matrix}CO\cdot NH\\ \quad\ \ |\\ N{=}CMe\end{matrix}.$$

This compound crystallises from alcohol in almost colourless, four- or six-sided plates, turns brown at 280° without previously melting, and gives rise to salts, which are not well characterised, with the exception of the methyl salt, which melts at 165°; and may also be obtained by acting on ethyl nitracetamidobenzoate with ammonia.

Ethyl nitracetylmethamidobenzoate [$COOEt : NMeAc : NO_2 = 1 : 2 : 5$] forms large, colourless plates, and melts at 66°. On heating with alcoholic or aqueous ammonia, it furnishes *ethyl* nitromethamidobenzoate and ammonium nitromethamidobenzoate respectively.

The formation of the above-described compounds shows that the action of ammonia on the derivatives of the ethyl salts of nitrohydroxybenzoic acids is determined both by the relative position of the substituted groups in the nucleus, and by the temperature. In the case of the metanitrobenzoates, no acid amide is formed, whilst in that of the paranitrobenzoates, acid amides are readily formed. In the case of ethyl metanitro-orthoethoxybenzoate, only the ethoxyl attached directly to the nucleus is displaced by amidogen at 125°, whilst at 170—180° the ethoxyl of the carboxyl group is also replaced.

G. T. M.

Metanitrocoumarin. By C. TAEGE (*Arch. Pharm.*, **229**, 71—83).—Nitrocoumarin, $NO_2{\cdot}C_9H_5O_2$, obtained by the action of fuming nitric acid on coumarin, melted at 187°, but after sublimation between watch glasses this fell to 183°; Bleibtreu (*Annalen*, **59**, 191) gives the number as 170°. By oxidation with potassium permanganate in an alkaline solution, metanitrosalicylic acid was obtained, indicating that the carboxyl group is in the meta-position, and the nitrocoumarin is of the meta-type. Metamidocoumarin, $C_9H_7NO_2$, described by Frapoli and Chiozza (*Annalen*, **95**, 253), was more simply prepared by dissolving nitrocoumarin in aqueous ammonia, heating nearly to boiling, and adding ferrous sulphate solution until the precipitate appeared pure black; this was filtered hot, washed a few times with hot water, and the filtrate was allowed to remain, when needles of the amidocoumarin crystallised out. This compound melts at 164°; Frapoli found 168°. The platinochloride was analysed. Dibromometanitrocoumarin, $NO_2{\cdot}C_9H_5Br_2O_2$, was obtained by exposing powdered metanitrocoumarin in a thin layer to bromine vapour for some days. After washing with alcohol, and recrystallising from chloroform, the prisms obtained melted at 151°, dissolved readily in alcohol, chloroform, and ether, but with difficulty in carbon bisulphide and light petroleum. Nitrosalicylaldehyde (unsymmetrical, melting at 125°), when heated over the free flame with acetic anhydride and sodium acetate, is converted into metanitrocoumarin. J. T.

The Tannin of Algarobilla and Myrobalans. By G. ZÖLFFEL (*Arch. Pharm.*, **229**, 123—160).—The legumes of several Chilian plants of the genus *Cæsalpinia* have been employed in Europe for tanning and dyeing. Two tanning principles are found in algarobilla: one, occurring to the extent of 8 to 10 per cent., is the glucoside of gallotannic acid, and by hydrolysis yields gallic acid and dextrose; the other, occurring in much larger quantity, is a sugar-free tannic acid which readily decomposes into ellagic acid, $C_{14}H_6O_8 + 2H_2O$. This new ellagotannic acid, $C_{14}H_{10}O_{10}$, has already been obtained in an impure form by Löwe, from the fruit of myrobalan and divi-divi. The dextrose noted above yields glucosazone when treated with phenylhydrazine (compare Fischer, Abstr., 1885, 53). The molecule of ellagotannic acid contains five hydroxyl groups, replaceable by acetyl, and its constitution may be thus represented, $C_6H_2(OH)_3{\cdot}COO{\cdot}C_6H_2(OH)_2{\cdot}COOH$. Ellagic acid loses its water of crystallisation at 100°. This acid, when treated with acetic anhydride, yields a tetracetyl derivative, as Schiff also has shown. The tanning principle of myrobalans is also a mixture of gallotannic glucoside with a much larger amount of ellagotannic acid. In both algarobilla and myrobalans, gallic acid exists in small quantity; the former also contains a little oxalic acid. J. T.

Shikimic Acid. By J. F. Eykman (*Ber.*, **24**, 1278—1303).—Shikimic acid, $C_7H_{10}O_5$, the preparation of which has already been described (Abstr., 1886, 95), forms a white, crystalline powder consisting of slender needles, melts at 184°, and has a sp. gr. of 1·599 at 14°. It dissolves in 5·5 parts of water, and in 20 parts of ordinary alcohol, readily forming supersaturated solutions, but is almost insoluble in absolute alcohol, ether, and benzene; it has a sp. rotation of $-246·3°$, and a conductivity constant of 0·0071. The ammonium salt, which crystallises in rhombic sphenoïds ($a : b : c = 0·827 : 1 : 1·759$), has an even stronger rotatory power, and therefore these two substances are among the most powerfully active compounds at present known. The acid does not reduce silver or copper solutions, but immediately decolorises alkaline potassium permanganate.

When barium or calcium shikimate is heated to about 230°, it yields products which show the qualitative reactions of catechol and dihydroxybenzoic acid, whilst the acid on fusion with potash yields, in addition to these, two compounds which appear to be meta- and para-hydroxybenzoic acid. On distillation, the calcium salt yields considerable quantities of phenol, which is probably formed according to the equation $C_7H_{10}O_5 = C_6H_6O + CO_2 + 2H_2O$.

The anhydrides of fatty acids act upon shikimic acid at their boiling point with formation of tri-substituted derivatives, the triacetyl, tripropionyl, and tributyryl compounds having been prepared. They are all yellowish, amorphous substances which could not be obtained crystalline; the number of acid radicles present was determined by titration, and in every case the result agreed with the supposition that three such groups have entered the molecule. Hence shikimic acid must contain 3 hydroxyl groups, and as it must, from its pronounced monobasic character, also contain a carboxyl group, the condition of all 5 atoms of oxygen is accounted for. Attempts were made to obtain ethereal salts of the acid, and of its triacetyl and tributyryl derivatives, but in every case the etherification was only a partial one.

If shikimic acid is warmed with concentrated hydrochloric acid, partial carbonisation takes place; from the residue remaining on evaporation, ether extracts parahydroxybenzoic acid, which must be formed simply by the elimination of 2 mols. H_2O :—$C_7H_{10}O_5 - 2H_2O = C_6H_4(OH)·COOH$. Other products are formed at the same time, but could not be identified.

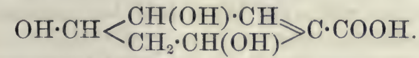
Sodium amalgam reduces an acidified solution of shikimic acid, forming *dihydroshikimic acid*, $C_7H_{12}O_5$. This is separated by neutralising the solution with soda, adding slightly less than an equivalent of hydrochloric acid, and a large quantity of alcohol. After filtering off precipitated sodium chloride, the remainder of the chlorine is removed by silver oxide, the lead salt of hydroshikimic acid precipitated by alcoholic lead acetate, and decomposed by hydrogen sulphide. The acid crystallises with great difficulty in hemimorphic, monosymmetric prisms ($a : b : c = 1·637 : 1 : 0·976$; $\beta = 46° 0' 30''$), melts at 175° (uncorr.), and dissolves in 7 parts of water. It does not reduce silver or copper solutions, nor is it immediately oxidised by alkaline potassium permanganate. It dissolves in sulphuric acid on warming with evolution of carbonic oxide and formation of a brown solution, it has a sp. gr. of 1·47 at 9°, a conductivity constant of 0·0031, and a sp. rotation $[\alpha]_D = 18·2°$; in the amorphous condition, however, it has a rotation four times as great. The amorphous acid is converted by hydrochloric acid, at 100°, into benzoic acid, but the crystallised acid must be more strongly heated before the decomposition takes place. The reaction takes place according to the equation $C_7H_{12}O_5 = C_6H_5·COOH + 3H_2O$.

When an equivalent of bromine is added to a supersaturated solution of shikimic acid, the *dibromide*, $C_7H_{10}Br_2O_5$, is formed, and crystallises from alcohol in rhombic sphenoïds ($a : b : c = 0·933 : 1 : 1·010$). Its conductivity constant is about 100 times as large as that of shikimic acid, namely, 0·75, and it has a sp. rotation $[\alpha]_D = -58°$. It reduces copper solution, and is reconverted by zinc and acetic acid into shikimic acid; on warming its aqueous solution, or, better, by the action of the theoretical quantity of silver oxide, it loses hydrogen bromide, forming *bromoshikimolactone*, $C_7H_9BrO_5$, which is also contained in the alcoholic and ethereal mother liquors of the dibromide. It is quite neutral, dissolves in water and ordinary alcohol, melts at 235° (uncorr.), and has a sp. gr. of 1·965 at 11°, and a sp. rotation $[\alpha]_D = +22°$. It crystallises in hemimorphic hexagonal needles ($a : c = 1 : 2·4595$), and scarcely reduces copper solutions, but forms silver bromide on heating with silver nitrate.

When the bromolactone is treated with baryta-water, it is converted into *dihydroxyshikimic acid*, $C_7H_{12}O_7$, which crystallises in long, monosymmetric needles ($a : b : c = 2·021 : 1 : 1·407$; $\beta = 74° 4'$), melts at 156° with formation of a lactone, is optically inactive, and has a conductivity constant 25 times as great as that of shikimic acid, namely, 0·072.

The author has also made certain observations with regard to quinic acid, $C_7H_{12}O_6$, and quinide, $C_7H_{10}O_5$, which are closely allied in constitution to shikimic acid. The sp. rotation of the former was found, in agreement with Hesse, to be $[\alpha]_D = -43·8°$, and is therefore only one quarter of that found for shikimic acid, and varies much less with the concentration. Quinide was prepared according to Hesse's method (*Annalen*, **110**, 335), and was found to have the properties ascribed to it by him. As it is completely neutral and optically inactive, it cannot be identical with shikimic acid. On boiling with milk of lime, it yields a *calcium* salt $(C_7H_{11}O_6)_2Ca + 4H_2O$, which, with acids, forms an inactive quinic acid. This has a conductivity constant of 0·022, compared with 0·0277 for the active acid.

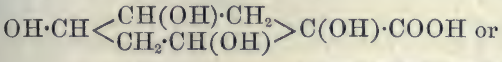
The above results in the case of shikimic acid, although from lack of material not as complete as is desirable, show that it must be a *trihydroxytetrahydrobenzoic acid*, $C_6H_6(OH)_3·COOH$. The position of the ethylene linkage and of the hydroxyl groups cannot be stated with certainty, but the author regards the following formula as the most probable:—



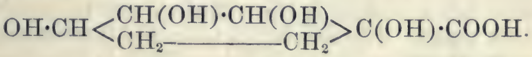
$$OH\cdot CH{<}\begin{matrix}CH(OH)\cdot CH\\ CH_2\cdot CH(OH)\end{matrix}{\geqslant}C\cdot COOH.$$

The stability of the compound towards alkalis renders it probable that the ethylene linkage is between the α- and β-carbon atoms (compare this vol., p. 452), and the above arrangement of the hydroxyl groups is the only one which readily explains the formation of the various benzene derivatives by the loss of water, unless the elimination takes place between groups in the para-position to one another, which is not at all probable. This formula is also in agreement with the relations between the conductivity constants of the different derivatives.

The constitution of quinic acid is regarded by the author as being probably represented by one of the following formulæ:—



$$OH\cdot CH{<}\begin{matrix}CH(OH)\cdot CH_2\\ CH_2\cdot CH(OH)\end{matrix}{>}C(OH)\cdot COOH \text{ or}$$



$$OH\cdot CH{<}\begin{matrix}CH(OH)\cdot CH(OH)\\ CH_2\text{———————}CH_2\end{matrix}{>}C(OH)\cdot COOH.$$

H. G. C.

4 : 5-Dichlorophthalic Acid: Derivatives of Ortho-xylene. By A. CLAUS and C. GRONEWEG (*J. pr. Chem.* [2], **43**, 252—259).—Experiments which will shortly be published show that the orientation of the dichlorortho-xylene which yields the dichlorophthalic acid melting at 183° (Abstr., 1885, 972) is $[Me_2 : Cl_2 = 1 : 2 : 4 : 5]$; the orientation of the acid is therefore also settled.

4 : 5-*Dichlorophthalic anhydride*, obtained by heating the acid at 130°, sublimes in long, colourless needles, and melts at 143° (uncorr.). The *potassium*, *sodium*, *ammonium*, *barium* (with 2 mols. H_2O), *calcium* (with 4 mols. H_2O), and *copper* salts are described. When the acid was distilled with the calculated quantity of soda-lime, it yielded a chlorobenzene which gave 4-nitro-1 : 2-dichlorobenzene (m. p. 43°) on nitration; this, taken in conjunction with the fact that neither of the chlorine atoms in this dichlorophthalic acid can be in the 3- or 6-position, is confirmatory of the above orientation.

4-Chloro-1 : 2-xylene boils at 195° (uncorr.), not 205° (Abstr., 1885, 972). 5-*Nitro*-4-*chloro*-1 : 2-*xylene*, obtained by mixing the chloro-xylene (1 vol.) with nitric acid, sp. gr. 1·5 (3—4 vols.) in the cold, and heating for half an hour on the water-bath, forms small needles which melt at 73° (uncorr.). 5-*Bromo*-4-*chloro*-1 : 2-*xylene*, obtained by brominating the chloro-xylene in chloroform in presence of iron, and distilling with steam, crystallises in long, colourless needles, and melts at 75° (uncorr.). *Nitro*-5-*bromo*-4-*chloro*-1 : 2-*xylene*, crystallises in small, colourless prisms, melts at 223° (uncorr.), and dissolves easily in acetone and in chloroform, sparingly in alcohol.

5-*Bromo*-4-*chlorophthalic acid* is obtained by heating the bromochloro-1 : 2-xylene with nitric acid (sp. gr. 1·1) for 5—6 hours in a sealed tube at 180—190°; it crystallises in aggregates of colourless, nacreous needles, melts at 205° (uncorr.), and is easily soluble in water, alcohol, and ether. The *anhydride* sublimes when the acid is heated at 120° in the form of small needles; it melts at 185° (uncorr.). The *sodium* salt (with 3 mols. H_2O) and *barium* salt (with 3 mols. H_2O) are described.

4 : 5-*Dichloro*-3-*bromo*-1 : 2-*xylene*, obtained by brominating dichlor-ortho-xylene (m. p. 237° ?) with bromine in presence of iron, forms slender, colourless, felted crystals which melt at 90° (uncorr.).

A. G. B.

Benzeneazomalonic Acid. By R. MEYER (*Ber.*, **24**, 1241—1245).—The author has already shown (Abstr., 1888, 369) that the benzeneazomalonic acid obtained from diazobenzene chloride and ethyl sodiomalonate is identical with the compound prepared from phenylhydrazine and mesoxalic acid. In place of the method previously given, the author recommends the following:—16 grams of ethyl malonate is dissolved in 250 c.c. of alcohol, a solution of 14 grams of crystallised sodium acetate in 62 per cent. alcohol added, and then gradually a well-cooled solution of diazobenzene chloride, containing an excess of ½ mol. hydrochloric acid, the temperature being kept below 0° during the addition, and the solution allowed to remain over night. The alcohol is then distilled off, solid soda added, and the precipitated sodium salt filtered off and decomposed with hydrochloric acid. To purify the acid it is dissolved in sodium carbonate solution, filtered, and the boiling solution again precipitated by hydrochloric acid. It then forms slender, yellow needles, melting at 163—164° with evolution of gas, which consists chiefly of carbonic anhydride and a little nitrogen, and also contains traces of ammonia and aniline. The *silver* salt, $PhN_2{\cdot}CH(COOAg)_2$, is a pale-yellow precipitate, and explodes on heating; it reacts very violently with ethyl iodide, and must be diluted with absolute alcohol in carrying out the reaction. The compound obtained is the *monethyl* salt, $PhN_2{\cdot}CH(COOH)(COOEt)$, which forms hair-like, yellow needles and melts at 114°. The author had hoped to obtain the *diethyl* salt, which would have one of the following formulæ, according as it is an azo-compound or a hydrazone,

$$NPh{:}N{\cdot}CH(COOEt)_2, \quad NHPh{\cdot}N{:}C(COOEt)_2,$$

and examine whether it still contained a hydrogen atom replaceable by metals, in which case the first formula must be correct, whereas if no such replacement took place the compound must have the hydrazone constitution. At present this remains an open question.

H. G. C.

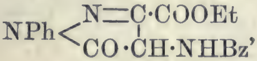
Ethyl Benzamidoxalacetate and Benzamidopyruvic Acid. By W. WISLICENUS (*Ber.*, **24**, 1257—1263).—When sodium ethoxide is added to a mixture of ethyl oxalate and ethyl hippurate, the action proceeds in the usual manner (Abstr., 1888, 1178), *ethyl sodiobenzamidoxalacetate*, $COOEt{\cdot}CNa(NHBz){\cdot}CO{\cdot}COOEt$, being formed. It crystallises out in yellowish crusts, which become pure white when washed with ether; its aqueous solution gives a precipitate with silver nitrate, which blackens and yields a mirror on warming. Free *ethyl benzamidoxalacetate* (*ethyl oxalhippurate*),

$$COOEt{\cdot}CH(NHBz){\cdot}CO{\cdot}COOEt,$$

is prepared by acidifying the aqueous solution of the sodium compound, extracting with ether, and evaporating in a vacuum. It is then obtained as an oil, which solidifies after a time; it crystallises from ether in slender, white, fascicular aggregates of needles, containing 1 mol. H_2O, which is partly evolved over sulphuric acid in a vacuum, with formation of the oily anhydrous ethyl salt. The hydrated compound melts at 73—74°, and gradually decomposes on continued heating, is readily soluble in hot water, ether, benzene, and alcohol, sparingly in light petroleum.

The crude ethereal solution in one instance deposited yellow crystals which melted at 164° with decomposition, had the composition $C_{13}H_{11}NO_5$, and gave a red coloration with ferric chloride in alcoholic solution. The constitution of this compound is unknown.

Ethyl benzamidoxalacetate readily yields a *hydrazone*, $C_{21}H_{23}N_3O_5$, which separates from ether in lustrous crystals, melts at 133—134°, and gives a deep violet coloration with ferric chloride in sulphuric acid solution. On boiling with acetic acid, it loses 1 mol. alcohol, and is converted into *ethyl phenylbenzamidopyrazoloncarboxylate*,



$$\mathrm{NPh}\Big<\begin{array}{l}\mathrm{N{=}C\cdot COOEt}\\ \qquad\;\;|\\ \mathrm{CO\cdot CH\cdot NHBz},\end{array}$$

which forms yellow crystals and melts at 194—195°. On boiling with aqueous soda, the benzoyl group is not eliminated, but simple hydrolysis takes place, the corresponding acid being formed; the latter forms slender, yellowish, matted needles, melts at 185—190° with decomposition, and is readily soluble in aqueous sodium carbonate, alcohol, and benzene, sparingly in water, ether, and light petroleum. The benzoyl group can only be eliminated by heating with hydrochloric acid at 160—170°, benzoic acid being then formed; the other products, however, form a resinous mass which could not be purified.

Ethyl benzamidoxalacetate is very readily decomposed by alkalis with formation of oxalic acid, hippuric acid and alcohol. On treatment with acids, however, an entirely different reaction takes place, benzamidopyruvic acid, alcohol, and carbonic anhydride being formed. The reaction is best carried out by treating the compound with fuming hydrochloric acid at the ordinary temperature, and allowing the mixture to remain for several days. The liquid is filtered from a little benzoic acid formed at the same time, and the filtrate evaporated in a vacuum; when a certain concentration is reached, the acid separates in reddish grains, which are purified by recrystallisation from ether. *Benzamidopyruvic acid*, $NHBz\cdot CH_2\cdot CO\cdot COOH$, forms white, flocculent masses, which when quickly heated melt at 195° with sudden decomposition, and on slowly heating at 190—192°. It is soluble in hot water, alcohol, and aqueous sodium carbonate, and with phenylhydrazine, yields a *hydrazone* which cannot be readily purified. Its solutions give a dark bluish-green coloration with ferric chloride, and precipitate silver and copper from their solutions. On heating with hydrochloric acid, benzoic acid is formed, but the author has been unable to isolate amidopyruvic acid from the other products. H. G. C.

Action of Iodine on Sodium Benzenesulphinate in the presence of Mercaptan. By R. Otto and J. Tröger (*Ber.*, **24**, 1145—1146).—The authors undertook these experiments in the hope of obtaining disulphoxides by the action of iodine on a mixture of mercaptan and an alkali sulphinate. This reaction does not, however, take place. An alcoholic solution of sodium benzenesulphinate and sodium phenyl mercaptan when treated with iodine yielded phenyl bisulphide and benzenesulphoiodide. Sodium benzenesulphinate and sodium ethyl mercaptan, treated in a similar way, gave ethyl bisulphide and benzene sulphoiodide. E. C. R.

Thioanhydrides of Aromatic Thiosulphonic Acids and Polythiosulphonic Acids. By R. Otto and J. Tröger (*Ber.*, **24**, 1125—1145).—*The Action of Iodine on Potassium Paratoluenethiosulphonate.*—When an aqueous solution of the thiosulphonate is mixed with a solution of iodine in aqueous potassium iodide until a slight excess of iodine is present, *toluenesulphothiosulphonic anhydride*, $(C_7H_7SO_2)_2S_2$, is formed. The mixture becomes milky, and a resinous compound is deposited, and is purified by extraction with ether; it crystallises from light petroleum in needles, sinters at 105°, and melts at 109°. This compound was the only product of the reaction: in all the other experiments a mixture was obtained of this compound and two others, namely, the *thioanhydride* of *toluenethiosulphonic acid*, $(C_7H_7SO_2)_2S$, and *toluenedisulphothiosulphonic anhydride*, $(C_7H_7SO_2)_2S_3$. For shortness sake these compounds are called the trithio-, the tetrathio-, and the pentathio-compound. Sulphonic acid and free sulphur are also formed by the action of iodine on the thiosulphonate; salts of toluenesulphonic acid were only obtained in insignificant quantity.

Potassium toluenethiosulphonate (40 grams) dissolved in water was gradually mixed with a 10 per cent. alcoholic solution of iodine (20 grams). The product is a white, crystalline mixture of the tetrathio- and pentathio-compounds with a little of the trithio-compound. By extraction with light petroleum, the trithio- and tetrathio-compounds are separated. The former is purified by crystallisation from alcohol, and melts at 133°. The product insoluble in light petroleum is crystallised from acetic acid, and yields the pentathio-compound which melts at 180—182°. Three other experiments gave a similar mixture. The tetrathio-compound is split up into the pentathio- and trithio-compounds when boiled for some time with acetic acid in a reflux apparatus. The trithio-compound (the thioanhydride of toluenethiosulphonic acid), $(C_7H_7SO_2)_2S$, is obtained by gradually adding a solution of iodine in potassium iodide to a solution containing potassium toluenesulphinate and potassium toluenethiosulphonate in molecular proportion. The product is purified by washing with a solution of potassium iodide and with water, and crystallisation from benzene. It melts at 133—134°. In a second experiment, the tetra- and pentathio-compounds were also obtained.

Action of Iodine on a mixture of Sodium Toluenesulphinate and Sodium Sulphide in molecular proportion.—W. Spring has stated that sodium thiosulphate is formed by the action of iodine on a mixture of sodium sulphite and sodium sulphide (*Ber.*, **7**, 1157). Hence it was of interest to study the action of iodine on a mixture of sodium toluenesulphinate and sodium sulphide. An alcoholic solution of iodine is gradually added to an aqueous solution of sodium sulphide and sodium toluenesulphinate in molecular proportion, until the yellow precipitate of sulphur which is first formed no longer redissolves; this shows that it no longer consists of sulphur, but of the thio-anhydrides of the thiosulphonic acid, that is, the products of the further action of iodine on the thiosulphonate first formed. The product was filtered, and the filtrate evaporated and extracted with alcohol. The alcoholic solution contains sodium toluenethiosulphonate. In a second experiment, enough iodine was added to convert all the thiosulphonate into thiosulphonic anhydride, and on crystallising the product from alcohol the trithio-compound (m. p. 134°) was obtained. Free sulphur was produced in all these experiments. From the production of free sulphur the authors conclude that the reaction takes place in two stages, as represented by the equations:—$Na_2S + I_2 = 2NaI + S$ and $C_7H_7SO_2Na + S = C_7H_7SO_2SNa$; and that the formation of sodium thiosulphate and sodium bisulphide observed by Spring is a similar reaction. For if a mixture of sodium sulphite and sodium sulphide in molecular proportion is carefully treated with an alcoholic solution of iodine, sulphur first separates, but redissolves on shaking or gently warming the mixture; and sulphur also separates when a small quantity of iodine solution is added to a solution of sodium sulphide.

Action of Chlorine on Potassium Toluenethiosulphonate.— When the thiosulphonate dissolved in water is treated with an excess of chlorine, the pentathio-compound mixed with the tri- and tetrathio-compounds is formed; and from the mother liquors toluenesulphonic acid and toluenesulphochloride are obtained.

The thioanhydride of paratoluenethiosulphonic acid, $(C_7H_7SO_2)_2S$, crystallises in the monosymmetric system,

$$a : b : c = 2{\cdot}8289 : 1 : 3{\cdot}2212;\ \beta = 60^\circ\ 7'.$$

The pentathio-compound, $(C_7H_7SO_2)_2S_3$, crystallises from hot ethyl acetate in small, pointed prisms of adamantine lustre, $a : b : c = 1 : 1 : 2{\cdot}732$. The crystals may belong either to the tetragonal or rhombic system.

The Action of Iodine on Potassium Benzenethiosulphonate.—An aqueous solution of the thiosulphonate is heated with a 10 per cent. alcoholic solution of iodine as long as precipitation takes place. The product is extracted with light petroleum and benzene, and the insoluble residue dissolved in acetic acid. The acetic solution deposited well-formed crystals of the *thioanhydride* of *benzenethiosulphonic* acid, $S(PhSO_2)_2$, melting at 133—134°. The petroleum extracts contain a mixture of the tetra- and pentathio-compounds, which could not be separated. Sulphuric acid and free sulphur are also formed in the reaction, as well as benzenesulphonic acid in inappreciable quantity. When potassium benzenethiosulphonate in aqueous solution is treated with chlorine, a product is obtained which smells faintly of benzenesulphochloride. On extraction with ether and crystallisation of the residue from alcohol, the pure *tetrathio-compound*, $(PhSO_2)_2S_2$, is obtained, and melts at 76—77°. The ethereal extract contains a mixture of the tetrathio- and pentathio-compounds. Sulphuric and benzenesulphonic acids are also formed, and are found in the aqueous liquors. The tetrathio-compound when boiled with acetic acid is split up into the trithio- and pentathio-compounds, and by fractional crystallisation from ethyl acetate, the latter can be obtained pure and melts at 101—102°. Two other experiments on the action of chlorine gave no trace of the tetrathio-compound, but only the penta- and trithio-compounds, together with a substantial quantity of benzene sulphochloride, and sulphuric and benzenesulphonic acids. When a solution of 50 grams of the thiosulphonate, cooled with ice, is chlorinated, 25 grams of product insoluble in water are obtained, and this consists almost entirely of the trithio-compound (m. p. 128—132°).

The thioanhydride of benzenesulphonic acid, $(PhSO_2)_2S$, crystallises in the monosymmetric system, $a : b : c = 2·8320 : 1 : 2·8280, \beta = 67°6'$. Plane of the optic axis parallel to the plane of symmetry. The tetrathio-compound, $(Ph·SO_2)_2S_2$, crystallises in very thin, transparent, lustrous plates belonging to the monosymmetric system,

$$a : b : c = 2·2740 : 1 : 1·7425,\ \beta = 61° 30'.$$

The pentathio-compound, $(Ph·SO_2)_2S_3$, crystallises in transparent, lustrous pyramids belonging to the tetragonal system, $a : b : c = 1 : 1 : 2·404$. They are hemihedral and are dextro-rotatory, $\omega = 1·7201$, $\epsilon = 1·7077$. Since this compound is isomorphous with the corresponding toluene derivative, the latter is also probably optically active, but the smallness of the crystals prevented the determination of the optical properties.

These thio-compounds dissolve easily in warm, aqueous potassium hydroxide, and also in aqueous potassium sulphide. The addition of hydrochloric acid to the solution precipitates sulphur, with formation of sulphinic acids. The pentathio-compound of toluene when heated with alcoholic ammonia in a sealed tube at 100° gives free sulphur and ammonium toluenethiosulphonate. Nascent hydrogen reduces the thioanhydrides to phenyl and tolyl mercaptans. The pentathio-compound when treated with metallic silver gives the disulphoxide, $C_7H_7SO_2·S·C_7H_7$, and the sulphonic anhydride, $(C_7H_7SO_2)_2O$. The latter is at once converted into the sulphonic acid.

Action of Iodine on a Mixture of Sodium Ethylsulphinate and Sodium Sulphide.—An aqueous solution of sodium sulphide and sodium ethylsulphinate in molecular proportion is carefully treated with an alcoholic solution of iodine in slight excess. A clear solution is obtained, from which ether extracts nothing. It contains sodium ethylthiosulphinate, which can be separated by evaporating to dryness and extracting with alcohol. When treated with zinc and hydrochloric acid, it yields ethyl mercaptan. Hydrochloric acid precipitates sulphur from the aqueous solution with production of sodium ethylsulphinate.
E. C. R.

Aromatic and Aliphatic Thiosulphonic Acids. By R. OTTO and A. RÖSSING (*Ber.*, **24**, 1147—1156).—*The Action of Ethyl Chlorocarbonate on Alkali Salts of Aromatic Thiosulphonic Acids.*—The authors have shown that ethyl chlorcarbonate acts on an alkali aromatic sulphinate with production of the ethyl salt of an aromatic sulphinic acid. The action of ethyl chlorcarbonate on thiosulphonates was studied in order to determine if disulphoxides, $R\cdot SO_2\cdot SC_nH_{2n+1}$, or the isomeric compounds $R\cdot SO\cdot SOC_nH_{2n+1}$ were produced. The reaction, however, takes place in quite a different way, and there are formed disulphoxides containing two similar aromatic residues, a sulphinic acid, ethereal salts of the sulphinic acid, and thioanhydrides of the thiosulphonic acid, with separation of carbonic anhydride and sulphur.

Potassium paratoluenethiosulphonate mixed with alcohol is gradually treated with a slight excess of ethyl chlorcarbonate: the mixture becomes acid. It is neutralised with potassium carbonate and the excess of ethyl chlorcarbonate neutralised with more thio-salt. The product is diluted with water and extracted with ether. The ethereal extract contains toluene disulphoxide, tolyl paratoluenethiosulphonate, ethyl toluenesulphinate, and a small quantity of the thioanhydride of toluenethiosulphonic acid. The residue, insoluble in water and ether, contains free sulphur, the thioanhydride of toluenedisulphothiosulphonic acid, $(C_7H_7SO_2)_2S_3$, and the trithio-compound. The aqueous liquors contain unaltered thiosulphonate and potassium toluenesulphinate. No gaseous products are evolved except carbonic anhydride. The authors put forward equations in explanation of this complicated reaction.

Potassium benzenethiosulphonate when treated with ethyl chlorcarbonate, behaves in an exactly similar way to the toluene salt.

Action of Phosphorus Pentachloride on Alkali Thiosulphonates.—Spring has stated that phosphorus pentachloride acts easily on sodium ethylthiosulphonate and yields a chloride which decomposes on heating, with separation of free sulphur, and when treated with caustic soda, yields the sodium thiosulphonate; so that its formula is probably EtS_2OCl. The authors, however, obtained a different result.

Potassium ethylthiosulphonate (2 mols.) is well mixed with phosphorus pentachloride (1 mol.) and the product poured into iced water. An oil is precipitated which is washed with very dilute potassium carbonate and dissolved in ether, and the product, after distilling off the ether, dried in a vacuum over sulphuric acid. The oily product contains only 3 per cent. of chlorine, which shows that very little chloride is present. When treated with aqueous potassium hydroxide, potassium ethylthiosulphonate is obtained. The explanation of this result is obtained on studying the products of the action of phosphorus pentachloride on potassium benzenethiosulphonate. The product of the action of phosphorus pentachloride on the latter salt is influenced by the proportions of the two compounds and also by the temperature. Phosphorus pentachloride first acts like free chlorine and phosphorus trichloride; potassium chloride and the thioanhydride of benzenethiosulphonic acid, $(PhSO_2)_2S_2$, are formed; the latter, as stated in the foregoing paper, easily splits up into the pentathio- and trithio-compounds. When the product is treated with potassium hydroxide, potassium benzenethiosulphonate is formed.

The authors conclude that the product obtained from potassium ethylthiosulphonate consists of compounds analogous to those obtained from salts of aromatic thiosulphonic acids. E. C. R.

Synthesis of Indigo from Phenylglycocine. By L. Lederer (*J. pr. Chem.* [2], **43**, 303—304).—This constitutes the author's concluding remarks in the controversy between himself and Heumann as to priority.

Non-Formation of an Indigo Derivative by Fusing Paratolylglycocine with Alkalis. By K. Heumann (*Ber.*, **24**, 1346).—Pure paratolylglycocine does not yield dimethylindigo on fusion with potassium hydroxide, as stated by Eckenroth (this vol., p. 722), and thus forms a remarkable exception to several other aromatic glycines which have been investigated by the author (this vol., p. 837).

A. R. L.

Isatin-blue. By C. Schotten (*Ber.*, **24**, 1366—1373).—*Dipiperidylisatin*, $C_{18}H_{25}N_3O$, is prepared by heating an alcoholic solution of isatin (10 grams) with 2 molecular proportions of piperidine for an hour on the water-bath; the crystals formed are collected and washed with alcohol; a further quantity is obtained on adding water to the alcoholic filtrate; the yield is 15 grams. It crystallises from alcohol in colourless, flat prisms, does not decompose at 100°, and is sparingly soluble in cold alcohol, less so in ether, and almost insoluble in benzene and chloroform. It gives a blood-red solution with mineral acids, and, later, decomposes into isatin and piperidine, but is only resolved into the latter by alkalis, on heating; it dissolves in glacial acetic acid with decomposition, and production of a green colour. If it is heated to 100° and the temperature slowly raised to 150°, a blue colour is produced, piperidine in about 1 molecular proportion is eliminated, and ultimately a brown, crystalline compound is formed; whilst if it is quickly raised to a temperature between 125° and 160°, isatin-blue (see below) is produced.

Isatin-blue is prepared by shaking dipiperidylisatin with several times its weight of acetic anhydride in a closed flask, at the ordinary temperature or at 60°, pouring into water, collecting, and washing with water: it is also formed when dipiperidylisatin is heated with acetic anhydride and absolute ether in a sealed tube at 100°. It is a blue powder, which separates from glacial acetic acid in microscopic, dichroic prisms; a streak on a glass plate appears blue by transmitted and yellow in reflected light; it decomposes at 230°, a brown oil passing over; it is moderately soluble in glacial acetic acid, forming a deep-blue solution, less so in ether and alcohol, and insoluble in benzene and chloroform. Its solution in glacial acetic acid shows a very strong band between wave-lengths 655 and 628, and except beyond the red there is a weak continuous absorption; on standing, another band is observed between wave-lengths 589 and 580, which is, however, due to the decomposition of the compound. The band observed with a solution of indigo sulphate is between wave-lengths 643 and 616, but the latter shows a much stronger continuous absorption in the violet than isatin-blue. A compound dissolving in ether with a purple-red colour is formed when a solution of the new colouring matter in glacial acetic acid is allowed to remain, or more quickly when heated; also when dipiperidylisatin is treated with acid chlorides or anhydrous formic acid. Isatin-blue is readily decomposed by mineral acids, but may be boiled for some time with alcoholic potash before the colour of the solution changes to red; on distilling with the latter, however, piperidine passes over, and a brownish-red compound, sparingly soluble in alcohol, and not showing the indophenin reaction, remains behind. When dipiperidylisatin (2 mols.) is treated with acetic anhydride, piperidine (3 mols. about) is obtained, and this leads to the formula $C_{21}H_{17}N_3O_2$ for isatin-blue, whilst the values obtained by the elementary analysis of the latter agree with the formula $C_{36}H_{30}N_5O_4$; its formation and constitution are therefore obscure, but it may be related to or identical with the colouring matter obtained by V. Meyer (Abstr., 1884, 587), and by Ciamician and Silber (*ibid.*, 740), by the action of pyrroline on isatin; it also resembles indin and isatopurpurin. The author is investigating the action of piperidine on quinone and quinol.

A. R. L.

Benzidinedisulphonic Acid. By H. LIMPRICHT (*Annalen*, **261**, 310—338).—The author has prepared a number of derivatives of benzidinedisulphonic acid, $\overset{2}{S}O_3H\cdot\overset{1}{C}_6H_3(\overset{4}{N}H_2)\cdot\overset{1}{C}_6H_3(\overset{4}{N}H_2)\cdot\overset{2}{S}O_3H$; the preparation of this acid, which was at first thought to be hydrazobenzenedisulphonic acid, has been previously described (Abstr., 1889, 399; compare also Abstr., 1890, 987).

When benzidinedisulphonic acid (10 grams) is dissolved in soda, the solution mixed with sodium nitrite (2 grams), then gradually treated at 0° with dilute sulphuric acid and kept for several days in the cold, the *diazo*-compound, $SO_3H\cdot C_6H_3(NH_2)\cdot C_6H_3<\substack{SO_3\\ -N}>N$, is deposited in reddish-yellow crystals, together with benzidinedisulphonic acid and the tetrazo-derivative; if, however, the solution is allowed to get warm during the process, the tetrazo-compound alone is formed. As the diazo-compound was not obtained in a pure condition, and many of the substances described below were prepared from this impure diazo-compound, and as, moreover, no special precautions were taken to free them from benzidinedisulphonic acid, &c., they cannot be regarded as pure chemical compounds.

Hydroxyamidodiphenyldisulphonic acid,

$$SO_3H\cdot C_6H_3(OH)\cdot C_6H_3(NH_2)\cdot SO_3H,$$

is formed when the crude diazo-compound is boiled with water, and can be isolated by means of its barium salt; it is a soft, yellow substance, very readily soluble in water and alcohol. The *barium* salt, $C_{12}H_9NS_2O_7Ba + 7$ or $8H_2O$, crystallises in small, efflorescent, reddish needles or prisms, is readily soluble in water, and loses the whole of its water at 175—180°. The potassium salt and the lead salt crystallise in long, efflorescent, colourless prisms, and are readily soluble in water.

Bromamidodiphenyldisulphonic acid can be prepared by boiling the crude diazo-compound with copper bromide or with concentrated hydrobromic acid; the *barium* salt, $C_{12}H_8S_2O_6NBr$, crystallises in small, efflorescent needles, is moderately easily soluble in hot water, and loses its water at 160°.

Hydrazineamidodiphenyldisulphonic acid was obtained, but only in a very impure condition, by reducing the crude diazo-compound with stannous chloride and hydrochloric acid; it is a pale yellow, crystalline compound, only sparingly soluble in hot water. The *barium* salt, $C_{12}H_{11}N_3S_2O_6Ba + 4H_2O$, forms small, lustrous crystals. When the acid is boiled with copper sulphate, it is converted into *amidodiphenyldisulphonic acid*, the *barium* salt of which forms small, efflorescent crystals, having the composition $C_{12}H_9NS_2O_6Ba + 4H_2O$.

The *tetrazo*-compound, $C_{12}H_6N_4S_2O_6 + 2H_2O$?, is deposited in yellow crystals when benzidinedisulphonic acid (25 grams) is treated with sodium nitrite (10·2 grams) and sulphuric acid, as described above, and the solution then kept for some days in a cool place (compare Balentine, Abstr., 1880, 809); it is very unstable, and therefore its composition could not be accurately determined. The *hydrobromide*, $C_{12}H_6N_4S_2O_6,HBr + 2H_2O$, prepared by treating dihydrazinediphenyldisulphonic acid with bromine in alcoholic solution, crystallises in reddish-yellow plates, is insoluble in alcohol, and is decomposed by water, yielding the tetrazo-derivative.

Dihydrazinediphenyldisulphonic acid is obtained when the tetrazo-compound is reduced with stannous chloride in the cold; it crystallises in yellowish prisms (with 2 mols. H_2O ?), and is only very sparingly soluble in hot water and insoluble in alcohol, ether, and chloroform. The *barium* salt, $C_{12}H_{12}N_4S_2O_6Ba$, seems to crystallise with 3 mols. H_2O, of which two are expelled at 110°.

Diphenyldisulphonic acid, $SO_3H\cdot C_6H_4\cdot C_6H_4\cdot SO_3H$ is formed when the preceding compound is boiled with copper sulphate, and when the tetrazo-compound is boiled with finely-divided copper and 95 per cent. alcohol; it is a syrup. The *barium* salt (with 6·5 mols. H_2O) forms large, transparent, efflorescent prisms, and is readily soluble in water, but only sparingly in alcohol. The *lead* salt (with 5 mols. H_2O) crystallises in efflorescent needles, and is very readily soluble in water. The potassium salt crystallises in four-sided prisms, and is readily soluble. The *chloride*, $C_{12}H_8S_2O_4Cl_2$, crystallises from chloroform in small, colourless prisms, melts at 138°, and is readily soluble in ether, benzene, and chloroform. The *amide*, $C_{12}H_8S_2O_4(NH_2)_2$, crystallises from alcohol or water, in both of which it is readily soluble, in four-sided, colourless prisms, containing 2 mols. H_2O, and softens at about 300°. The *anilide*, $C_{12}H_8S_2O_4(NHPh)_2$, separates from alcohol in small, colourless crystals melting at 157°.

Dinitrodiphenyldisulphonic chloride, $C_{12}H_6S_2O_4Cl_2(NO_2)_2$, is obtained when the chloride just described is treated with a mixture of fuming nitric acid and concentrated sulphuric acid; it crystallises from chloroform in small rhombohedra and melts at 202°. The corresponding *amide* forms yellow, well-defined, rhombic plates, and does not melt below 260°.

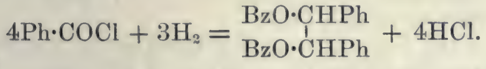
Diphenol, $C_{12}H_8(OH)_2$ [= 2 : 2′], is formed when diphenyldisulphonic acid is fused with alkalis; it forms large, transparent prisms, melts at 99°, and is probably identical with the compound (m. p. 98°) obtained from fluorene by Hodgkinson and Matthews (Trans., 1883, 163).

Diphenoldisulphonic acid can be obtained by boiling the tetrazo-derivative of benzidinedisulphonic acid with water (40 parts) (compare Brunneman, Abstr., 1880, 807); it is a crystalline compound, readily soluble in water. The *barium* salt (with 2 mols. H_2O) and the lead salt (with 4 mols. H_2O) form well-defined crystals and are soluble in water. The *tetranitro*-derivative is formed when the acid is evaporated with nitric acid; its *sodium* salt (with 1 mol. H_2O) and *potassium* salt are yellow, crystalline compounds.

F. S. K.

Isobenzile. By H. Klinger and O. Standke (*Ber.*, **24**, 1264—1271).—Isobenzile may be prepared by the following method more readily than by the one previously given (Abstr., 1883, 920; 1886, 888):—900 grams of sodium amalgam (2·5 per cent.) is covered with 150 c.c. of dry ether, and 100 grams of benzoic chloride gradually added with constant cooling. After an hour, the product is placed in warm water and kept boiling for 36 hours, care being taken to exclude moisture. The yellow or yellowish-brown solution is then filtered, well shaken with sodium carbonate solution to remove benzoic acid and chloride, the ether distilled off, and the residue allowed to remain in a vacuum. The crystals which separate are collected and washed with a little ether; they consist of isobenzile mixed with a little of the compound melting at 242—244°, the formation of which was previously observed by Klinger (Abstr., 1883, 920). This is separated by recrystallising from hot alcohol and finally from cold ether, in which the high melting compound is sparingly soluble. Isobenzile crystallises well from acetic acid, forming lustrous, compact crystals, and melts 3° higher than formerly stated, namely, at 159°. It decomposes partially on boiling, forming benzoic anhydride.

It has already been shown that isobenzile is converted by bromine into benzile and benzoic bromide, and by nitric acid into benzile and benzoic acid, from which it would appear to be the benzoate of an alcohol containing the group $PhC\cdot CPh$, which is formed by the reduction of benzoic chloride, and then further acted on by the excess of the latter. This view was confirmed by the fact that the compound melting at 242—244° is *hydrobenzoïn dibenzoate*, which must be formed in the following manner:—



$$4Ph\cdot COCl + 3H_2 = \begin{array}{c} BzO\cdot CHPh \\ | \\ BzO\cdot CHPh \end{array} + 4HCl.$$

It is also readily obtained by the action of silver benzoate on stilbene dibromide.

By the action of alcoholic potash, isobenzile is resolved into benzoïn and benzoic acid, and it must, therefore, be *diphenylacetylene dibenzoate*, $\begin{array}{l} PhC\cdot OBz \\ \ \ \| \\ PhC\cdot OBz \end{array}$, the corresponding diphenylacetylene glycol first formed by the hydrolysis passing at once into the tautomeric benzoïn,

$$OH\cdot CHPh\colon COPh.$$

This formula is in agreement with the molecular weight found by Raoult's method, and readily explains the action of bromine and nitric acid on isobenzile, the benzoïn first formed being oxidised to benzile.

By the action of hydrochloric acid on isobenzile the authors obtained benzoic acid and benzile, instead of benzoïn as expected. This result is accounted for by Klingemann's observation, that benzoïn itself is for the most part converted into benzile by the action of hydrochloric acid.

Attempts to synthesise isobenzile from tolane dibromide and silver benzoate have been made without success. H. G. C.

New Synthesis of Isobenzile. By H. KLINGER and L. SCHMITZ (*Ber.*, **24**, 1276—1277).—By the action of sodium wire (3·3 grams) on a solution of benzoic chloride (20 grams) and benzaldehyde (15·1 grams) in anhydrous ether, a yellow solution is obtained, which on filtering leaves a residue of hydrobenzoïn dibenzoate, sodium chloride, and sodium benzoate. The ethereal solution on evaporation leaves a residue which is distilled in a current of steam and treated with sodium carbonate solution to remove benzaldehyde, benzyl alcohol, and benzoic acid; the pasty residue is then recrystallised from acetic acid, and yields a mixture of hydrobenzoïn benzoate and isobenzile; these are separated by means of alcohol and ether. The yield of isobenzile is not good; in its formation, it is possible that benzaldehyde and benzoic chloride unite directly, forming the compound $CHPhCl·OBz$, 2 molecules of which then combine, with loss of hydrogen chloride and formation of isobenzile. H. G. C.

Naphthoic Acids. By Å. G. EKSTRAND (*J. pr. Chem.* [2], **43**, 409—432; compare Abstr., 1889, 52, 152, and this vol., p. 77).—*Nitro-β-naphthoic Acid.*—The *ethyl* salt of this acid is present in small quantity in the mother liquor from which the previously described nitronaphthoic acids (this vol., *loc. cit.*), are obtained, and crystallises from a solution of the mixed ethyl salts in acetic acid in the form of nodules, which, on repeated crystallisation from alcohol, give rhombic plates melting at 92°. The free acid crystallises in small, colourless needles, melts at 279°, and is readily soluble in alcohol; the *calcium* salt crystallises with 7 mols. H_2O, and is only slightly soluble in water. On reduction with ferrous sulphate in ammoniacal solution, the acid furnishes an *amido-β-naphthoic acid*, which crystallises from dilute alcohol in needles melting at 211°.

In addition to the four nitro-β-naphthoic acids specified, a fifth appears to be formed amongst the products of nitration. The author has not succeeded in isolating the free acid, but has obtained the *ethyl* salt in the form of long, hard, colourless needles; it melts at 131°.

Chloro-β-naphthonitrile, $C_{10}H_6Cl·CN$, obtained on chlorination of a cold solution of β-naphthonitrile in acetic acid containing iodine, melts at 144°, and is converted into the crystalline *amide*, $C_{10}H_6Cl·CONH_2$ (needles melting at 186—187°), on boiling with alcoholic potash, until ammonia commences to be evolved.

Chloro-β-naphthoic acid is conveniently prepared by digesting the above-mentioned nitrile (m. p. 144°) with alcoholic potash in a reflux apparatus; it crystallises from alcohol and acetic acid in colourless needles, and melts at 263°. The *ethyl* salt melts at 45°; the sodium salt crystallises with 2 mols. H_2O, and the *barium* and *calcium* salts with 4½ mols. H_2O and 3½ mols. H_2O respectively. The acid has most probably the constitution [COOH : Cl = 2 : 1′] or [COOH : Cl = 2 : 4′].

Chloronitro-β-naphthoic acid is obtained by heating chloro-β-naphthoic acid (m. p. 263°) with excess of nitric acid of sp. gr. 1·42. On cooling the clear solution, the acid separates in the form of slender needles, which, on recrystallisation from acetic acid, give a pure, colourless product; this melts at 271°. The *ethyl* salt melts at 118°; the *calcium* salt crystallises with 5 mols. H_2O, and is only sparingly soluble in water.

Chlorodinitro-β-naphthoic acid is formed on warming the chloro-β-naphthoic acid (m. p. 263°) with red, fuming nitric acid in presence of a small quantity of concentrated sulphuric acid. It crystallises in long, flat needles, melts at 243°, and gives an *ethyl* salt forming brownish needles and melting at 132°.

Chlorotrinitro-β-naphthoic acid is obtained on warming in a water-bath a mixture of chloro-β-naphthoic acid (m. p. 263°) with a large excess of fuming nitric acid mixed with an equal volume of concentrated sulphuric acid. It crystallises from warm acetic acid in hard, yellow, apparently octahedral crystals, and melts with decomposition at 260—261°. The *ethyl* salt crystallises in needles which melt at 188°; and the *calcium* salt in golden-yellow needles containing 2 mols. H_2O.

Chloro-β-naphthoic acid is obtained on diazotising the amido-β-naphthoic acid melting at 219°. It crystallises in slender, white needles, and melts at 260°. The *ethyl* salt is not well characterised; the *barium* salt crystallises in needles and contains 6 mols. H_2O; and the *calcium* salt crystallises in nodular aggregates containing 7 mols. H_2O.

Dichloro-β-naphthonitrile is formed when a hot solution of β-naphthonitrile in acetic acid containing iodine is treated with excess of chlorine. It crystallises in needles, melts at 140°, is only sparingly soluble in alcohol; and, when cautiously heated with alcoholic potash, forms the *amide*, $C_{10}H_5Cl_2 \cdot CONH_2$, which crystallises in slender, colourless needles, and melts at 218°. If the heating with potash be continued, dichloro-β-naphthoic acid (m. p. 291°) is produced, and this is identical with the acid obtained on direct chlorination of β-naphthoic acid in hot acetic acid solution containing iodine. The *ethyl* salt crystallises from alcohol in long needles, and melts at 66°; the *potassium salt* (1 mol. H_2O) and the *barium* salt (4 mols. H_2O) both crystallise in colourless needles, and are well characterised; the *calcium* salt (2½ mols. H_2O) forms small prisms which are only slightly soluble in water (1 part in 3018). This acid is also the chief product of further chlorination of both the chloro-β-naphthoic acids m. p. 263° and m. p. 260° respectively, and must, therefore, have the constitution [Cl_2 : COOH = 1′ : 4′ : 2]. On oxidation with potassium permanganate, it appears to give a mixture of dichlorophthalic acid (75—80 per cent.) and trimellitic acid (20—25 per cent.).

Dichlorodinitro-β-naphthoic acid is obtained on heating dichloro-β-naphthoic acid (m. p. 291°) with a mixture of fuming nitric acid and concentrated sulphuric acid in a water-bath, until the solid is nearly all dissolved. On crystallisation from acetic acid, it forms rhombic plates and melts at 283°. The *ethyl* salt melts at 128°; the *calcium* salt crystallises with 6 mols. H_2O.

On nitrating dichloro-β-naphthoic acid (m. p. 291°) with nitric acid of sp. gr. 1·42, at least two nitrodichloro-derivatives, both crystallising in needles, and melting at 247° and 261° respectively, are formed. In this respect dichloro-β-naphthoic acid resembles β-naphthoic acid.

Dichloro-β-naphthoic acid is obtained by first reducing and then diazotising the dinitro-β-naphthoic acid melting at 226°. It crystallises in needles, melts at 282°, gives an *ethyl* salt melting at 72°, and a sodium salt and a calcium salt, both crystallising in needles and containing 2 mols. H_2O and $3\frac{1}{2}$ mols. H_2O respectively.

Dichloro-β-naphthoic acid obtained from the dinitro-acid giving the diamido-acid melting at 248° crystallises in needles, melts at 254°, and gives an *ethyl* salt melting at 86—87°.

Bromo-β-naphthoic acid, obtained by the action of bromine on β-naphthoic acid suspended in water, crystallises in colourless needles, melts at 258°, and gives an *ethyl* salt crystallising in long, white needles melting at 53—54°. These characteristics differ from those ascribed to the compound by Hausemann (this Journal, 1876, i, 599).

G. T. M.

Alizarinsulphonic Acids; Conversion of Anthraquinone-α- and β-disulphonic Acids into Flavopurpurin and Anthrapurpurin. By R. E. Schmidt (*J. pr. Chem.* [2], **43**, 232—237).—The author brings forward evidence to show that the intermediate products obtained during the conversion of anthraquinone-α- and -β-disulphonic acids into flavopurpurin and anthrapurpurin, respectively, by fusion with sodium hydroxide, are alizarinsulphonic acids (compare Graebe and Liebermann, *Annalen*, **160**, 139; Perger, *J. pr. Chem.* [2], **8**, 159). They both dye mordanted wool, and can be obtained directly from alizarin; the latter fact is of technical importance, because the best yield of these acids which can be obtained by melting the anthraquinonedisulphonic acids with sodium hydroxide is not more than 30 per cent., it being difficult to stop the fusion at the right moment. The process is patented by F. Bayer and Co.; it consists in acting on alizarin or the "usual alizarinsulphonic acids" with sulphuric anhydride (5—10 mols.) in the form of anhydrosulphuric acid of 25—30 per cent., until a portion of the mixture gives a not very intense, dirty colour on dissolving it in ice-cold water and adding sodium hydroxide. The alizarindisulphonic acids thus formed, unlike alizarinsulphonic acids, are not precipitated by sodium chloride, but are entirely thrown out by potassium chloride. To convert the disulphonic acids into the monosulphonic acids, they are heated with sulphuric acid (60° B.) in an open vessel at 180°. This mixture of alizarinsulphonic acids when melted with potassium hydroxide yields flavopurpurin and anthrapurpurin in almost equal proportions.

It is commonly stated in chemical literature that anthraflavic and isoanthraflavic acids are intermediate products in the preparation of flavopurpurin and anthrapurpurin; they are not so, but only bye-products. Anthraflavic acid remains unaltered when fused with alkalis in presence of oxygen.

A. G. B.

New Dyes of the Anthraquinone Series. By R. E. SCHMIDT and L. GATTERMANN (*J. pr. Chem.* [2], **43**, 237—252).—In this abstract, a paper by Schmidt and a succeeding one by Gattermann are embodied. The colouring matters here described have been patented by F. Bayer and Co.

"Alizarinbordeaux," $C_{14}H_4O_2(OH)_4$, is prepared by acting on alizarin (1 part) with 70—80 per cent. anhydrosulphuric acid (10 or more parts) at 25—50° for four days, and then pouring the mixture into melting ice. An *acid sulphate*, $C_{14}H_4O_2(OH)_2{:}O_2{:}SO_2$, is thus obtained as an orange precipitate which crystallises from glacial acetic acid in lustrous leaflets; it is dissolved in an alkali, and the solution acidified and heated, whereby "alizarinbordeaux" is precipitated. "Alizarinbordeaux" can be distilled unchanged; it crystallises from nitrobenzene in brilliant, red needles having a green, metallic lustre; its *acetyl derivative*, $C_{14}H_4O_2(OAc)_4$, forms bright-yellow needles melting at 200°. The crystalline form and optical properties of "alizarinbordeaux" show that it is identical with Liebermann's quinalizarin; its constitution is therefore $[(OH)_4 = 1:2:1':4']$ (compare this vol., p. 463).

The dyeing properties of the product are described; it is characteristic of it that it dissolves in strong sulphuric acid with a bluer colour than that of the original substance, a property not possessed by alizarin. In its behaviour to reagents it resembles alizarin. *Nitroquinalizarin*, $NO_2\cdot C_{14}H_3O_2(OH)_4$, crystallises from nitrobenzene in brilliant, dark needles with a green, metallic lustre; by reduction, it yields an *amido-derivative.* By the action of stannous chloride on an alkaline solution of quinalizarin and subsequent acidification, a reduction product is formed which crystallises from glacial acetic acid in brilliant, brownish-red leaves.

Quinalizarin is also obtained when quinizarin is treated with sulphuric anhydride in the manner described above.

By oxidising quinalizarin with manganese dioxide in sulphuric acid, "alizarincyanin R.," $C_{14}H_3O_2(OH)_5$, is obtained; it crystallises from nitrobenzene in bronze-coloured leaves, and can be distilled unchanged; the *acetyl derivative* is described.

Hexahydroxyanthraquinone, $C_{14}H_2O_2(OH)_6$, is obtained when sulphuric acid acts on quinalizarin at 200°, or sulphuric anhydride on anthraquinone at 30°; it forms dark-green crystals.

A new *tetrahydroxyquinone*, crystallising in green needles, is obtained when anhydrosulphuric acid acts on purpurin. In all these reactions, the sulphuric anhydride acts as an oxidising agent, being reduced to sulphurous anhydride.

Reference is made to the production of several other new dyes, but they do not appear to have been chemically investigated.

A. G. B.

Massoyene. By O. WALLACH (*Arch. Pharm.*, **229**, 116—120; compare Abstr., 1890, 638 and 1316).—The author still maintains that massoyene does not exist in massoya rind, but that the oil from this rind contains a relatively large quantity of pinene with limonene and perhaps dipentene.

J. T.

Oil of Polei. By E. BECKMANN and M. PLEISSNER (*Annalen*, **262**, 1—37).—Spanish oil of Polei, from *Mentha pulegium*, is a light yellow or green, rather thick liquid with an odour recalling that of peppermint. On fractionating the oil (62 grams), under the ordinary atmospheric pressure, considerable decomposition takes place; a small portion (3 grams), consisting principally of water, passes over below 212°, the principal portion (50 grams) between 212° and 216°, and a small quantity of a dark-yellow liquid (4 grams) between 216° and 223°, leaving a brownish residue (5 grams).

A compound of the composition $C_{10}H_{16}O$, named by the author *pulegone*, can be isolated from the portion boiling at 212—216° by repeated fractional distillation under reduced pressure (60 mm.); it is a colourless liquid, of sp. gr. 0·9323 at 20°, boils at 130—131° (60 mm.), and has an odour recalling, but distinct from, that of oil of peppermint. Its specific rotatory power is $[\alpha]_D = 22·89$, but this value is slightly diminished when the oil is treated with sulphuric acid or distilled with steam, probably owing to resinification. Pulegone quickly turns yellow, even when kept in closed vessels, and it does not solidify when cooled in a mixture of ice and salt; it is gradually resinified by hot alcoholic potash, and it does not give an ethereal salt with benzoic or stearic anhydride; it gives some, but not all, the reactions of aldehydes, and with phenylhydrazine it yields only oily or resinous, very unstable compounds. Molecular weight determinations gave results in accordance with those required by the molecular formula $C_{10}H_{16}O$; its molecular refractive power was found to be $M_D = 45·55$, whereas the value calculated for the formula $C_{10}H_{16}O''$ is $M_D = 45·82$.

Pulegoneoxime, $C_{10}H_{19}NO_2$, can be obtained by treating pulegone with hydroxylamine in boiling alcoholic ethereal solution; it crystallises from ether in long needles, melts at 157° with decomposition, and is only sparingly soluble in cold alcohol, benzene, and light petroleum; its specific rotatory power is $[\alpha]_D = -83·44$. Molecular weight determinations showed that the compound has the molecular formula given above. Pulegoneoxime is more readily soluble in dilute acids than menthoneoxime, and, unlike the latter, it is not acted on by cold sulphuric acid of sp. gr. 1·17; it dissolves freely in hydrochloric acid, yielding a solution which gradually turns brown, but it is only very sparingly soluble in alkalis. It reduces ammoniacal solutions of silver and copper on warming. The *hydrochloride*, $C_{10}H_{19}NO_2,HCl$, separates from alcoholic ether in well-defined rhombic crystals, $a : b : c = 0·6048 : 1 : 1·0477$, melts at 117—118° with decomposition, and is readily soluble in water; its specific rotatory power is $[\alpha]_D = -32·43°$. The *benzoyl* derivative, $C_{10}H_{18}O{:}N{\cdot}OBz$, prepared by treating the oxime with benzoic chloride in ethereal solution, crystallises from dilute alcohol in colourless needles melting at 137—138° with decomposition. The *acetyl* derivative, $C_{10}H_{18}O{:}N{\cdot}OAc$, is formed when the oxime is warmed with acetic chloride; it crystallises in long needles, and melts at 149°.

Pulegoneamine, $C_{10}H_{19}ON$, is obtained when the oxime is treated with hydriodic acid, and the crystalline hydriodide obtained in this way warmed with excess of the concentrated acid; it is a yellowish oil having a bitter taste and an amine-like odour, and it decomposes when heated; it is only sparingly soluble in water, but readily in ether and alcohol. The *hydrochloride*, $C_{10}H_{19}NO,HCl$, was prepared, but only in an impure condition, by treating the base with hydrogen chloride in ethereal solution; it crystallises from alcohol in long needles, melts at 117°, and is readily soluble in water, alcohol, benzene, and glacial acetic acid, but only moderately easily in light petroleum, and sparingly in ether. *Pulegoneamine phenylthiocarbimide*, $C_{10}H_{18}O\colon N\cdot CS\cdot NHPh$, is precipitated in colourless plates on warming a benzene solution of pulegoneamine with phenylthiocarbimide; it melts at 198°. The *benzoyl* derivative, $C_{10}H_{18}O\colon NBz$, separates from warm, dilute alcohol in colourless, feathery crystals, melts at 100·5—101°, and is sparingly soluble in water, ether, and benzene, but readily in alcohol. The *methyl* derivative, $C_{10}H_{18}O\colon NMe$, prepared by boiling the amine with methyl iodide, and decomposing the product with potash, is a light-yellow oil; its *platinochloride*, $(C_{11}H_{21}NO)_2,H_2PtCl_6$, crystallises in well-defined yellow needles, and is sparingly soluble in alcohol and ether. When pulegoneamine is boiled with concentrated potash, it is decomposed into pulegone and ammonia; methylpulegoneamine, under the same conditions, yields pulegone and methylamine.

An additive compound of the composition $C_{10}H_{17}BrO$ is deposited in colourless crystals when hydrogen bromide is passed into a well-cooled solution of pulegone in light petroleum; it separates from dilute alcohol in well-defined, colourless crystals, melts at 40·5°, and is readily soluble in alcohol and ether. It gradually decomposes on keeping, and it is converted into pulegone by freshly-precipitated silver oxide and lead hydroxide, but it is not acted on by cold dilute soda or by warm sodium carbonate; its specific rotatory power is $[\alpha]_D = -33{\cdot}88°$. When treated with hydroxylamine, as described in the preparation of pulegoneoxime, it is converted into a compound which crystallises in quadratic plates, melts at 38°, and has probably the composition $C_{10}H_{18}BrNO$; on keeping this substance for some time, it first changes into a mass of needles melting at 110°, which are free from bromine, but contain nitrogen, and then into pulegoneoxime. When the additive compound is reduced with zinc-dust in alcoholic solution, it yields very small quantities of pulegone and a considerable quantity of an oil, which has the same molecular formula as, and possesses all the properties of, the levomenthone described by Beckmann (Abstr., 1889, 721), except that its oxime melts at a higher temperature, namely, at 84—85°; when this isomeride of menthone is treated with sodium in ethereal solution, it is converted into a mixture of isomeric menthols, from which a considerable quantity of the benzoyl derivative of natural lævomenthol can be isolated in a crystalline condition. Lævomenthol is also obtained, together with resinous products, when pulegone is reduced with sodium under the same conditions.

The author gives three possible formulæ for pulegone.

F. S. K.

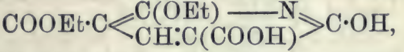
Saponin. By O. HESSE (*Annalen*, **261**, 371—378).—A study of the literature of saponin and of senegin (Bolley, *Annalen*, **90**, 211; Christophsohn, *Arch. Pharm.*, **206**, 432, 481, 503) leads to the conclusion that the two compounds are identical, and that the supposed varieties of saponin obtained from various Caryophyllaceæ represent one and the same compound. According to Rochleder (*Wiener Acad. Ber.*, **56**, 97), saponin, on hydrolysis, is converted into glucose (3 mols.) and a compound of the composition $C_{14}H_{22}O_2$, for which the author proposes the name *sapogenol;* assuming that sapogenol has the above composition, and that the hydrolysis takes its normal course, the composition of saponin is represented by the formula $C_{32}H_{52}O_{17}$ ($= C_{14}H_{22}O_2 + 3C_6H_{12}O_6 - 3H_2O$).

The analytical results obtained by Stütz (*Annalen*, **218**, 231) in studying saponin and its derivatives are more in accordance with this view of the composition of the compound than with that of Stütz, who concluded that the glucoside had the composition $C_{19}H_{30}O_{10}$; assuming that the composition of saponin is expressed by the formula $C_{32}H_{52}O_{17}$, the tetracetyl, $C_{19}H_{26}Ac_4O_{10}$, tetrabutyl, $C_{19}H_{26}Bu_4O_{10}$, pentacetyl, $C_{19}H_{25}Ac_5O_{10}$, and heptacetyl, $C_{19}H_{25}Ac_5O_9(OAc)_2$, derivatives described by Stütz must be regarded as the heptacetyl, $C_{32}H_{45}Ac_7O_{17}$, heptabutyl, $C_{32}H_{45}Bu_7O_{17}$, octacetyl, $C_{32}H_{44}Ac_8O_{17}$, and dodecacetyl, $C_{32}H_{40}Ac_{12}O_{17}$, derivatives respectively, and the compound to which Stütz gave the formula $C_{19}H_{25}Ac_5O_8(OAc)_4$ as a compound of the composition $C_{32}H_{40}Ac_{15}O_{22}$, and a derivative of saponin trihydrate, $C_{32}H_{58}O_{20}$; the existence of a mono- and of a di-hydrate of saponin is also not improbable.

The formation of sapogenin, saponetin, and saporetin (senegenin), by the decomposition of saponin, can be easily expressed by simple equations, proceeding on the assumption that the formula $C_{32}H_{52}O_{17}$ is correct. F. S. K.

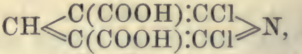
Poisonous Constituents of "Timbó." By F. PFAFF (*Arch. Pharm.* [2], **29**, 31—48).—*Timbó* is the name given in Brazil to several plants such as *Serjania cuspidata*, St. H., *Serjania lethalis*, and *Paullinia pinnata* of the order Sapindacæ, and *Tephrosia toxicaria* and *Physallis heterophylla* of the order Leguminosæ, all of which are used for the purpose of stupefying fish. A decoction of the root is preferred as affording the more powerful poison. To isolate the active principle, an alcoholic extract of the plant was concentrated, washed with water, treated with ether, and the dark-coloured ethereal solution decolorised by means of sodium carbonate and dilute soda solution. After removing the ether and drying over sulphuric acid, solid crude timboïn was obtained, which softened when exposed to the air. A similar product was obtained by precipitating the alcoholic extract with lead acetate, and purifying the filtrate. Further treatment of the crude product with alcohol, light petroleum, and benzene or chloroform at length yielded a hard, yellowish-white, sandy substance, which, under the microscope, clearly indicates crystalline structure. *Timboïn*, $C_{27}H_{26}O_8$, melts at 83°, is very soluble in ether, alcohol, benzene, glacial acetic acid, toluene, and carbon bisulphide, exceedingly soluble in chloroform; very sparingly soluble in light petroleum, and almost insoluble in water. Its alcoholic solution is not precipitated either by normal or basic lead acetate, iodine solution, or tannin. Its solution in acetic acid or in alcohol gives a white, flocculent precipitate with water; but these solutions give no coloration, either with ferric chloride or potassium chromate. The compound becomes first black and then reddish-brown with concentrated sulphuric acid. Sobieranski considers timboïn to be a chemically neutral, indifferent substance, and a nerve poison of the toxine class. *Anhydrotimboïn*, $C_{27}H_{24}O_7$, was obtained as slender, coloured, needle-shaped crystals during the refining of the crude timboïn. It was also produced directly from timboïn by heating the alcoholic solution with hydrochloric acid. This compound melts at 215—216°, and is not poisonous. Light petroleum, boiling at 38—40°, extracted from the crude timboïn an oily compound, *timbol*, $C_{20}H_{16}O$, probably also a poisonous compound, occurring chiefly in the stem and branches of the plants. J. T.

Synthesis of Pyridine Derivatives from Derivatives of α-Pyrone. By M. GUTHZEIT and O. DRESSEL (*Annalen*, **262**, 89—132).—The authors discuss at some length the mechanism of the reactions which take place in the conversion of α-pyrone into pyridine derivatives, more especially as regards the formation of ethyl hydrogen ethoxyhydroxypyridinedicarboxylate from ethyl ethoxy-α-pyronedicarboxylate they arrive at the conclusion that the simplest and most probable explanation of such reactions is that the pyrone derivative first combines with the elements of ammonia to form an intermediate product, which is then converted into a pyridine derivative by the elimination of 1 mol. H_2O.

Ethyl hydrogen ethoxyhydroxypyridinedicarboxylate (*ethyl ethoxy-α-pyridonedicarboxylate*),  $\mathrm{COOEt{\cdot}C}\left\langle\begin{matrix}\mathrm{C(OEt)}\text{———}\mathrm{N}\\ \mathrm{CH{:}C(COOH)}\end{matrix}\right\rangle\mathrm{C{\cdot}OH}$, is obtained when ethyl ethoxy-α-pyronedicarboxylate, prepared as previously described (Abstr., 1889, 860), is shaken with 4—5 per cent. ammonia, and the filtered solution acidified with hydrochloric acid. It crystallises from a mixture of acetone and ether in colourless needles, melts at 159—160°, and is moderately easily soluble in acetone, alcohol, and glacial acetic acid, but more sparingly in ether and water, and almost insoluble in benzene, light petroleum, and carbon bisulphide. Molecular weight determinations by Raoult's method in glacial acetic acid solution gave results in accordance with those required by the molecular formula given above. The *silver* salt, $C_{11}H_{12}O_6NAg$, is a crystalline, moderately stable compound, very sparingly soluble in water. The *acetyl* derivative, $C_{13}H_{15}O_7N$, is formed when the ethyl hydrogen salt is heated with acetic anhydride at 130°; it melts at 99—100°, is freely soluble in cold benzene, and is readily decomposed by warm water.

Ethyl ethoxyhydroxypyridinedicarboxylate, $C_{13}H_{17}O_6N$, can be prepared by treating an alcoholic solution of the ethyl hydrogen salt with hydrogen chloride, but it is more easily obtained by decomposing the silver salt with ethyl iodide; it crystallises from alcohol and benzene in needles, melts at 80—81°, and is soluble in dilute ammonia and dilute sodium carbonate. When the ethyl hydrogen salt is heated above its melting point, carbonic anhydride (1 mol.) is evolved and there remains a brown oil, which consists principally of ethyl ethoxyhydroxypyridinedicarboxylate, identical with the compound described above, and a basic substance which is probably α-ethoxy-α-hydroxypyridine, but which could not be isolated in a pure condition. Ethoxyhydroxypyridinedicarboxylic acid (compare Abstr., 1889, 860) separates from water in crystals containing 1 mol. H_2O, and melts at 181—182° with evolution of carbonic anhydride (2 mols.) yielding a brown oil which probably consists for the most part of ethoxyhydroxypyridine; when heated with concentrated hydriodic acid at 130°, it gives ethyl iodide, and when heated with fuming hydrochloric acid at 180°, it yields ethyl chloride, ammonia, and glutaconic acid (m. p. 133—134°).

Citrazinic acid undergoes a decomposition similar to that observed in the case of ethoxyhydroxypyridinedicarboxylic acid; when it is heated at 180° with hydrochloric acid, it yields ammonia and aconitic acid, together with carbonic anhydride, which is produced by the decomposition of some of the aconitic acid. The relationship between citrazinic acid and ethoxyhydroxypyridinedicarboxylic acid is also shown by their behaviour on reduction with tin and hydrochloric acid in the manner described by Behrmann and Hofmann in the case of citrazinic acid; the last-named compound yields tricarballylic acid under these conditions, ethoxyhydroxypyridinedicarboxylic acid giving glutaric acid.

αα-Dichlorodinicotinic acid,  $CH{<}\begin{matrix}C(COOH){:}CCl\\C(COOH){:}CCl\end{matrix}{>}N$, is obtained when anhydrous ethoxyhydroxypyridinedicarboxylic acid is mixed with phosphorus pentachloride and phosphorus oxychloride, the mixture heated at 240—250° for 5—6 hours, and the product decomposed with ice-cold water; it separates from ether in colourless crystals, melts at 230° with evolution of carbonic anhydride, and is readily decomposed by warm water yielding dihydroxydinicotinic acid. It is moderately easily soluble in ether and alcohol, but more sparingly in cold water; it dissolves freely in dilute ammonia, the neutral solution giving with silver nitrate and with lead acetate a colourless, with ferric chloride a yellow, and with copper acetate a green, precipitate. The *ethyl* salt, $C_{11}H_{11}Cl_2NO_4$, is easily obtained by treating the chloride of the acid with alcohol; it crystallises in compact, monoclinic prisms, melts at 75—76°, and is readily soluble in ether, alcohol, chloroform, benzene, glacial acetic acid, and hot light petroleum, but more sparingly in cold light petroleum; it is quickly decomposed by sodium ethoxide in warm alcoholic solution with separation of sodium chloride. When the dichloro-acid is heated with concentrated hydriodic acid at 180°, it is converted into dinicotinic acid (m. p. 322°); the formation of this acid from ethyl hydrogen ethoxyhydroxypyridinedicarboxylate by the series of reactions described above is a conclusive proof that the ethyl hydrogen salt has the constitution assigned to it. F. S. K.

Betaïnes of Pyridine Bases. By M. Krüger (*J. pr. Chem.* [2], **43**, 271—303 and 364—377; compare Abstr., 1890, 1431).—There are four methods of obtaining betaïnes: (1) Hofmann's, by the action of ethyl chloracetate on the tertiary base, producing the chloride of the alkyl betaïne; (2) Liebrich's, by the action of chloracetic acid on the tertiary base at a raised temperature, producing the betaïne hydrochloride; (3) Griess', by the action of methyl iodide and an alkali on the amido-acid in methyl alcohol, producing the alkaline iodide of the betaïne; (4) Kraut's, by the action of an alkyl iodide on the silver amido-salt, producing the iodide of the alkyl betaïne.

Ethyl pyridinebetaïne chloride, $C_5H_5NCl\cdot CH_2\cdot COOEt$, obtained by Hofmann's reaction and purified by extraction with ether, in which it is insoluble, forms a rose-coloured, crystalline powder; it melts at 100° to a yellowish-red liquid of peculiar odour, and decomposes with blackening at 110—115°; it is very soluble in water, alcohol, and chloroform. The *platinochloride* forms lustrous, orange-red, rhombic leaflets and decomposes at 213°; the *aurochloride* crystallises in thin, yellow leaflets and melts at 117°; the *mercurochloride* forms microscopic, white, four-sided prisms which melt at 124—125°; the *cadmiochloride*, $C_9H_{12}NO_2Cl,CdCl_2$, crystallises in long, lustrous needles which aggregate to an opaque white mass at 141°; the *cadmiochloride*, $(C_9H_2NO_2Cl)_2,CdCl_2$, crystallises in vitreous, rhombic leaflets and melts at 107°. To convert ethyl pyridinebetaïne chloride into pyridinebetaïne, it is treated with silver oxide and water, silver chloride and alcohol being formed. Ethyl pyridinebetaïne does not exist; its *nitrate* was obtained by decomposing the chloride with silver nitrate.

Pyridinebetaïne hydrochloride has been described by v. Gerichten (Abstr., 1882, 1109); its platinochloride melts at 211°, its aurochloride at 165°; the reactions of this base with the usual reagents for alkaloïds are here given. The *hydrobromide* crystallises in rhombic leaflets and decomposes at 198—200°. The *nitrate*, obtained from the chloride by the action of silver nitrate, forms vitreous, colourless leaflets which melt at 145° with decomposition. The *sulphate* is similarly prepared; it crystallises in colourless leaflets and decomposes at 175°. The *chromate*, $C_7H_7NO_2,CrO_3$, forms a yellow, crystalline precipitate and explodes about 166°. The *picrate* crystallises in microscopic four-sided prisms with oblique ends, and melts at 142—143°. The *argentonitrate* and *bismuthoiodide* are also described (compare Abstr., 1890, 1431).

The author finds that the product of the action of chloracetic acid (20 grams) on pyridine (10 grams) is a mixture of normal and basic pyridinebetaïne hydrochloride (compare Abstr., 1882, 1109), which is easily converted into the pure normal salt by adding a slight excess of hydrochloric acid. The crystallography of the normal hydrochloride is given. *Basic pyridinebetaïne hydrochloride*, $(C_7H_7NO_2)_2,HCl,H_2O$, separates from a hot alcoholic solution of the mixture before the normal salt in large, broad, vitreous, colourless crystals which are well developed on one side only and become opaque in air without change of composition; when quickly recrystallised it separates as long, slender prisms; it melts at 159° with decomposition, and dissolves in water and hot alcohol, but not in ether; its aqueous solution is acid. The *mercurochloride*, $2C_7H_7NO_2,HCl,H_2O,4HgCl_2$, crystallises in colourless, lustrous leaflets which melt at 134°.

Basic pyridinebetaïne hydrobromide, is obtained from the normal hydrobromide by evaporating a solution of the latter with excess of pyridine on the water-bath; it crystallises in long, broad leaflets, or slender, needle-shaped prisms, and decomposes at 170°; its aqueous solution is acid. Both the basic and normal hydrobromides are formed when pyridinebetaïne (5 grams) is heated in a sealed tube with bromine (4 grams) and water (20 c.c.) at 100°; when the bromine is in excess, only the normal salt is formed.

By heating pyridinebetaïne hydrochloride at comparatively low temperatures, pyridine is produced; but at 230—240°, or when treated with strong organic bases, a more deep-seated reaction takes place. By oxidation with potassium permanganate, the betaïne is entirely converted into pyridine.

When sodium amalgam acts on a warm solution of pyridinebetaïne, a blue colour is developed; this changes to purple-violet on cooling, and to brown after some hours; heating restores the blue colour; when the amalgam acts on a cold, not alkaline solution of pyridinebetaïne, an amorphous yellowish-white precipitate is obtained, and the filtrate from this becomes blue on the addition of more sodium amalgam. The same colour reaction is observed with ethyl pyridinebetaïne chloride, but no precipitate is obtained. The amorphous substance is at first yellowish-green, but becomes black when dried at 100°; analyses are given, but no formula is deduced. From the filtrate from this substance, a base was obtained which gave a platinochloride melting at 224—225° and agreeing in properties with the platinochloride of Coppola's pyridinecholine (Abstr., 1886, 76); that the new base is pyridinecholine was further proved by preparing the latter, when it was found to give the same colour reactions.

In Hesekiel's recipe for preparing β-picoline (Abstr., 1885, 812; 1886, 256), 24 hours digestion is unnecessary, 6—8 being sufficient; the author's product boiled at 141—143°.

β-Picolinebetaïne hydrochloride, $C_6H_7NCl{\cdot}CH_2{\cdot}COOH$, obtained by warming β-picoline with chloracetic acid (equal mols.), crystallises from alcohol in long, broad, four-sided, vitreous, colourless prisms; it melts at 189° with decomposition, and dissolves in hot alcohol and water but not in ether; when precipitated by ether from alcoholic solution, it is a white, crystalline, deliquescent powder. Its reactions with several alkaloïdal reagents are given. The *platinochloride* crystallises in small, six-sided, orange-red tables and decomposes at 222°.

β-Picolinebetaïne is obtained by decomposing the hydrochloride with moist silver oxide and evaporating; by adding ether to the solution of the residue in alcohol and stirring with a glass rod, the base is precipitated in microscopic, rhombic leaflets (with 1 mol. H_2O). The *basic hydrochloride*, $2C_8H_9NO_2,HCl,H_2O$, separates when a solution of the normal hydrochloride and the base (equal mols.) in hot alcohol is cooled, in small, thick crystals. When a hot alcoholic solution of pyridinebetaïne and β-picolinebetaïne hydrochloride (equal mols.) is cooled, a *double salt*, $C_8H_9NO_2,HCl,C_7H_7ON_2,H_2O$, crystallises in thin, rectangular leaflets.

Ethyl β-picolinebetaïne chloride is obtained when β-picoline and ethyl chloracetate interact over potassium hydroxide; after several days, the crystallised mass is extracted with ether, which leaves the new compound as a rose-coloured, crystalline powder; it decomposes at 153° and is very hygroscopic. The *platinochloride* forms yellow, four-sided prisms and decomposes at 207°. When Kahlbaum's artificial picoline was acted on by ethyl chloracetate and the solution of the product precipitated by platinum tetrachloride, the above described salt was obtained; this method will serve to separate β-picoline from its isomerides in artificial picoline.

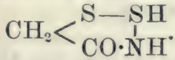
Ethyl ethylpiperidinebetaïne chloride, $C_7H_{15}NCl\cdot CH_2\cdot COOEt$, obtained by the action of ethyl chloracetate on ethylpiperidine, crystallises in very thin, lustrous leaflets. The *platinochloride* crystallises in thin, feebly lustrous, orange-yellow, rhombic leaflets and melts at 150°.

Ethylpiperidinebetaïne is obtained by acting on the above chloride with moist silver oxide, alcohol being formed at the same time; it crystallises in small leaflets, soluble in water and alcohol, but insoluble in ether. The *hydrochloride* is obtained by the action of chloracetic acid on ethylpiperidine; the product is dissolved in alcohol and precipitated by ether, when microscopic, long, four-sided prisms separate; it is very hygroscopic and melts at 186—187° with decomposition; the *platinochloride* and some of the reactions with alkaloïdal reagents are described.

A summary of the general reactions of these betaïnes concludes the paper. A. G. B.

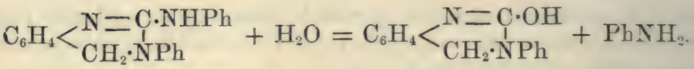
Constitution of Rhodanic Acid. By A. Miolati (*Annalen*, **262**, 82—88).—Rhodanic acid can be obtained (1) by heating thiohydantoïn with excess of carbon bisulphide in alcoholic solution, (2) by warming ethyl chloracetate with an alcoholic solution of ammonium dithiocarbamate and hydrochloric acid, and (3) by treating ethyl thiocyanoacetate with hydrogen sulphide in alcoholic solution; it crystallises in yellowish prisms and melts at 166—167° with decomposition.

These syntheses of the "acid" show that it is an α-keto-μ-thiothiazolidine of the constitution

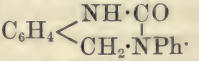


$CH_2<\begin{matrix} S\text{—}SH \\ | \\ CO\cdot NH \end{matrix}$. F. S. K.

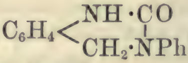
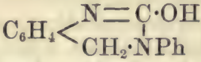
Quinazolines. By C. Paal and A. Bodewig (*Ber.*, **24**, 1157—1161).—Orthonitrobenzoylaniline and phenyl cyanate, when brought together, give a theoretical yield of orthonitrobenzyldiphenylcarbamide. The authors attempted to obtain anilidophenyldihydroquinazoline by reduction of the latter compound. The reaction, however, takes place in a different way, and they obtained a feeble base of the composition $C_{14}H_{12}N_2O$, together with aniline. The production of this new base is due to the action of water on the unstable phenylamidophenyldihydroquinazoline, as expressed in the equation



$$C_6H_4<\begin{array}{l}N=C\cdot NHPh\\ CH_2\cdot\overset{|}{N}Ph\end{array} + H_2O = C_6H_4<\begin{array}{l}N=C\cdot OH\\ CH_2\cdot\overset{|}{N}Ph\end{array} + PhNH_2.$$

Söderbaum and Widman (Abstr., 1889, 972), by treating orthohydroxytolylphenylcarbamide with hydrochloric acid, have obtained a compound to which they give the name benzophenyldihydroketometadiazine, and the formula  $C_6H_4<\begin{array}{l}NH\cdot CO\\ CH_2\cdot\overset{|}{N}Ph\end{array}$. It is entirely different from the former base.

Orthonitrobenzyldiphenylcarbamide, $C_{20}H_{17}N_3O_3$, is obtained by heating orthonitrobenzylaniline and phenyl cyanate in molecular proportion at 120°. It crystallises from alcohol in white leaflets or tablets, melts at 124—125°, and is easily soluble in most organic solvents, with the exception of petroleum. When cautiously warmed with alcoholic potash, it splits up into symmetrical diphenylcarbamide (m. p. 233°) and an amorphous compound, which the authors consider to be formed by the action of excess of alkali on the orthonitrobenzyl alcohol, which is first produced.

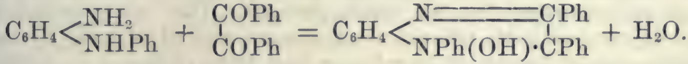
3′-Phenyl-2′-ketotetrahydroquinazoline,  $C_6H_4<\begin{array}{l}NH\cdot CO\\ CH_2\cdot\overset{|}{N}Ph\end{array}$, or *3′-phenyl-2′-hydroxydihydroquinazoline*,  $C_6H_4<\begin{array}{l}N=C\cdot OH\\ CH_2\cdot\overset{|}{N}Ph\end{array}$, is obtained by treating orthonitrobenzyldiphenylcarbamide in alcoholic solution with tin and hydrochloric acid. On adding excess of concentrated hydrochloric acid, the stannochloride, $C_{14}H_{12}N_2O,HCl,SnCl_2$, crystallises out, and aniline remains in solution. The salt is finely ground and decomposed with ammonium sulphide, and the base extracted with alcohol. It crystallises in white needles, melts at 170°, and is easily soluble in benzene, moderately in alcohol and ether, and almost insoluble in light petroleum. An attempt to reduce the base in alcoholic solution with sodium failed.

The isomeric base, *benzophenyldihydroketometadiazine*, $C_{14}H_{12}N_2O$, is obtained as described by Söderbaum and Widman. It crystallises in white, lustrous plates or flat needles, and melts at 144—145°.

The authors point out that the two bases $C_{14}H_{12}N_2O$, which from their method of formation ought to have the same constitution, are entirely different in properties. They are engaged in investigating the cause of this difference. E. C. R.

Action of Dioxyquinones on Orthodiamines. By R. NIETZKI and G. HASTERLIK (*Ber.*, **24**, 1337—1340).—Dioxyphenazine is prepared by the action of dioxyquinone on orthophenylenediamine hydrochloride; the acetyl derivative melts at 226°, not at 230° as stated by O. Fischer and Hepp. Corresponding compounds are obtained from orthotoluylenediamine and 1 : 2-naphthylenediamine. Kehrmann's imide formula for the eurhodoles and eurhodines, whilst facilitating the classification of the eurhodines, oxazines, and saffranines, is probably incorrect, since it is incompatible with the production of eurhodoles by fusion of azinesulphonic acids with alkalis, as observed by O. N. Witt; the formation of eurhodine diazo-compounds also tells against the formula, as does the fact that the diacetyl derivatives are readily and completely hydrolysed by dilute alkalis, whereas if one acetyl group were linked to oxygen, and the other to nitrogen, the former would probably be readily eliminated, but the latter only with difficulty; hence a monacetyl derivative should be capable of being isolated, which is not the case. J. B. T.

Azonium Compounds. By F. KEHRMANN and J. MESSINGER (*Ber.*, **24**, 1239—1241).—In a recent communication (this vol., p. 747), O. Fischer has shown that fluorescent colouring matters of the quinoxaline series may be obtained by the action of alkylated orthodiamines on α-ketonic alcohols or hydroxyquinones. The authors have found that the substituted orthodiamines also react readily with orthodiketones, forming the azonium compounds, from which the safranin dyes are derived. Thus, when alcoholic solutions of orthamidodiphenylamine and a slight excess of benzile are warmed with hydrogen chloride (1 mol.) on the water-bath, the product of the reaction saturated with ammonia and poured into water, a sulphur-yellow, crystalline precipitate is obtained, which, on recrystallisation from alcohol, forms well-developed sulphur-yellow prisms melting at 134—135°. It is readily soluble in alcohol, ether, and benzene, with a yellow colour and beautiful green fluorescence, has the composition $C_{26}H_{19}N_2{\cdot}OH$, and is formed in the following manner:—



$$C_6H_4{<}\begin{matrix}NH_2\\ NHPh\end{matrix} + \begin{matrix}COPh\\ |\\ COPh\end{matrix} = C_6H_4{<}\begin{matrix}N\equiv\equiv\equiv CPh\\ \qquad\qquad |\\ NPh(OH){\cdot}CPh\end{matrix} + H_2O.$$

Its solution, on the addition of hydrochloric acid, becomes momentarily red and then pure yellow, without fluorescence. Its *ferrichloride*, $C_{26}H_{19}N_2FeCl_4$, forms lustrous, golden-yellow, prismatic crystals, moderately soluble in cold water, its *platinochloride*, $(C_{26}H_{19}N_2)_2PtCl_6$, brownish-yellow, lustrous scales, almost insoluble in water and alcohol, and the *mercurochloride* canary-yellow scales. The *chloride*, *nitrate*, and *sulphate* are readily soluble in water, and have a yellow colour.

H. G. C.

Nicotine. By A. PINNER and R. WOLFFENSTEIN (*Ber.*, **24**, 1373—1377).—It is stated by Will (*Annalen*, **118**, 206) that nicotine reacts with benzoic chloride with the development of much heat, but when the latter is added to a solution of nicotine in anhydrous ether, a viscid substance separates, which after a time forms white, deliquescent crystals, resembling wavellite, of the composition $C_{12}H_{12}NOCl$: this he regarded as an additive compound, or as benzoylnicotine hydrochloride.

The authors have obtained a compound agreeing with the above description by dissolving nicotine (1 mol.) in ether rendered anhydrous by sodium, and adding benzoic chloride (2 mols.), but they find it to be *basic nicotine hydrochoride*, $C_{10}H_{14}N_2,HCl$; it is very soluble in water, and yields nicotine picrate (m. p. 218°; see *Ber.*, **24**, 65) on adding picric acid to its aqueous solution. When pyridine, dimethylaniline, and piperidine are similarly treated with benzoic chloride, crystalline substances consisting of the hydrochlorides and benzoates are formed. The production of these salts is due to the action of the moisture of the air on the benzoic chloride, whereby benzoic and hydrochloric acids are formed, the latter then reacting with the bases. When nicotine and benzoic chloride are dissolved in ether rendered anhydrous by phosphoric anhydride, and the mixture is kept in a closed flask over concentrated sulphuric acid, an oil separates which does not solidify if kept even for 14 days ; it was not further examined. But little heat is developed on mixing nicotine with benzoic chloride (2 mols.), and if the mixture is heated on the water-bath for 20 minutes, a thick syrup is obtained ; after washing this with water and dilute alkali, it is dissolved in dilute hydrochloric acid, and precipitated with ammonia ; the precipitate is extracted with ether, and the residue, after distilling off the latter, dissolved in alcohol and water added, whereby a syrupy mass is obtained. It appears to be a compound of 1 mol. of nicotine with 1 mol. of benzoic chloride ; it has basic properties ; on adding picric acid to a solution of the compound in dilute hydrochloric acid, the *picrate*, $C_{23}H_{22}N_5O_8Cl$, separates as an oil, which solidifies after a time, and then melts at 139°.

A. R. L.

Cytisine and Ulexine. By J. v. D. MOER and P. C. PLUGGE (*Arch. Pharm.* [2], **29**, 48—68).—The work done by Moer is communicated by Plugge. The finely-crushed seeds of *Cytisus laburnum* were extracted with cold water, and the solution was concentrated in winter by removing the ice which formed. The concentrated solution was treated with normal lead acetate and then with hydrogen sulphide ; after excess of the latter had been removed by warming, sodium hydroxide was added to distinctly alkaline reaction, when the application of chloroform removed the cytisine and yielded it, when concentrated and treated with ether, as a colourless, crystalline mass. Repeated treatment with chloroform and ether gave the pure alkaloïd. Cytisine, $C_{11}H_{16}N_2O$, forms colourless, odourless crystals melting at 150—151·5° (uncorr.). It is a strong base, soluble in all proportions in water, alcohol, and chloroform, insoluble in ether, light petroleum, carbon bisulphide, readily soluble in ethyl acetate ; benzene dissolves 1·26 per cent., and amyl alcohol dissolves 0·303 per cent. Cytisine dissolved in water has a rotatory power of $[\alpha]_D = -120°$. The value for other solutions is also given. On adding a solution of a ferric salt to the free alkaloïd, or one of its salts, a red coloration is produced ; on adding to this some drops of hydrogen peroxide solution, the colour disappears, followed immediately on warming by a blue colour. This is a very characteristic reaction, and will indicate 0·00005 gram. Platinum chloride precipitates the alkaloïd in not too dilute solutions. Precipitates are also produced by gold chloride, potassium mercuric iodide, iodised potassium iodide, phosphomolybdic acid, phosphotungstic acid (1 : 30000), tannic acid, and picric acid. Mercuric chloride precipitates the free base from its solutions, but not from solutions of its salts. The simple salts of cytisine are all soluble in water, and are easily soluble in absolute alcohol ; the nitrate is the least soluble in the latter liquid, and can be obtained from its solution therein in the form of large crystals. The composition of the following salts was found to be :—Cytisine nitrate, $C_{11}H_{16}N_2O,HNO_3 + H_2O$; platinochloride, $(C_{11}H_{16}N_2O)_2,H_2PtCl_6$; aurochloride, $C_{11}H_{16}N_2O,HAuCl_4$.

For the detection of cytisine in poisoning cases, Dragendorff's method can be applied, advantage being taken of the solubility of the alkaloïd in chloroform, and of the characteristic test given above. The vomit and urine should be first examined. Salts of the alkaloïd pass away in the urine within 24 hours, but if leaves or seeds have been employed, the expulsion may take a longer time. Moer compares the composition and properties of cytisine and ulexine and their compounds, and concludes that these two alkaloïds are identical (compare Partheil, this vol., p. 750). J. T.

Action of Alcohols and Aldehydes on Proteïds. By T. L. Brunton and S. Martin (*J. Physiol.*, **12**, 1—4).—Solutions of the following proteïds were used :—(1) egg-albumin, (2) serum-albumin containing a little serum-globulin, and (3) a mixture of proto- and deutero-albumose prepared from Witte's "peptone." The solution was dropped into six times its bulk of an alcohol or aldehyde, and the following points noted :—*a*. Whether the reagent precipitated the proteïd ; *b*. Whether the precipitate was rendered insoluble in distilled water, by the prolonged action of the reagent ; *c*. Whether any change of colour occurred in the precipitate. It was found that with egg-albumin, allyl alcohol was the most powerful precipitant and coagulant of the series. Methyl, ethyl, propyl, isobutyl, isopropyl, and tertiary butyl alcohols come next ; they are all active coagulators ; amyl alcohol is a partial coagulator ; and heptyl and octyl alcohols do not precipitate or in any way change the solution. Acetaldehyde and propaldehyde are about equal in coagulating power to ethyl alcohol, and turn the precipitated proteïd brown ; isobutaldehyde has a slower action, and does not turn the precipitate brown.

With serum-albumin, the results were very similar ; the alcohols may be arranged in the following order, the most active being placed first :—

1. Methyl, ethyl and propyl alcohols.
2. Isopropyl alcohol.
3. Tertiary butyl alcohol.
4. Isobutyl and amyl alcohols precipitate, but do not coagulate.
5. Heptyl alcohol does not precipitate.
6. The aldehydes previously mentioned neither precipitate nor coagulate albumin, but acetaldehyde and propaldehyde turn the solution brown.

With the albumose solution, allyl alcohol is the only one that precipitates and renders the precipitate insoluble. Methyl, ethyl, propyl, isopropyl, and tertiary butyl alcohols cause a precipitate ; isobutyl alcohol causes a cloudiness ; amyl, heptyl, and octyl alcohols have no effect whatever.

The general result obtained as to the effect of alcohols on proteïds is that the higher alcohols have a less powerful action in precipitating and coagulating proteïds than the lower ones. Allyl alcohol stands apart from the others as the most powerful precipitating and coagulating agent employed. W. D. H.

A Product of the Putrefaction of Proteïds. By S. GABRIEL and W. ASCHAN (*Ber.*, **24**, 1364—1366).—δ-Amidovaleric acid, prepared from benzoylpiperidine by C. Schotten (Abstr., 1888, 1104), and also by a synthetical method by S. Gabriel (Abstr., 1890, 1129), is identical with the compound obtained by the putrefaction of fibrin and flesh by E. and H. Salkowski (Abstr., 1883, 925). Neither of these compounds is poisonous; they dissolve copper oxide but not silver oxide, and give neither a precipitate nor a blue coloration with ammoniacal silver and copper acetate solutions respectively.

γ-Ethyl phthalimidopropylmalonate (Gabriel, *loc. cit.*) is prepared by dissolving sodium (3 grams) in alcohol (30 c.c.), adding ethyl malonate (21 grams) and γ-bromopropylphthalimide (30 grams), and heating the mixture in a reflux apparatus for 4 hours. The product is poured into water, the alcohol and unaltered ethyl malonate removed by a current of steam, and the oily residue extracted with ether; on evaporating the ethereal solution, a yellowish oil is left, which, after a time, solidifies to a crystalline cake; the yield is 80 per cent. of the theoretical.

δ-Amidovaleric acid aurochloride, $C_5H_{11}NO_2,HAuCl_4 + H_2O$, is obtained by heating the above ethyl derivative with hydrochloric acid (5 parts) at 170°, filtering off the phthalic acid, evaporating the filtrate, and adding a 20 per cent. auric chloride solution to the resulting hydrochloride dissolved in a little warm water; it separates in glistening, red crystals which probably belong to the monoclinic system, melts at 86—87°, and seems in all respects to be identical with that obtained by E. and H. Salkowski (*loc. cit.*). A. R. L.

Physiological Chemistry.

Influence of Bile on the Fat-splitting Properties of Pancreatic Juice. By B. K. RACHFORD (*J. Physiol.*, **12**, 72—94).—Some preliminary experiments on emulsions led to the following results:—No amount of stirring will give a permanent emulsion of neutral olive oil with either distilled water or 0·25 per cent. sodium carbonate solution; rancid olive oil, however, although it gives no emulsion with water, gives a good emulsion with the alkaline solution. In the formation of an emulsion, not only must the oil be broken into fine globules, but these must be prevented from running together, by a coating of soap or mucilaginous material. No mechanical emulsion, however, is as perfect as a physiological one. The influence of bile in emulsification is thus summarised:—Bile prevents the formation of an emulsion, probably by preventing the formation of soap membranes; if bile be added to an emulsion the moment after it is formed, the emulsion clears; but if a few minutes elapse before the addition of bile, there is no such clearing, the emulsion having become more stable. Acids similarly destroy emulsions, probably by destroying soaps.

Rabbits' pancreatic juice is alkaline, and remains active for many hours after removal from the body; if it be shaken with neutral olive oil, fatty acids are formed and the oil becomes acid; if too much acid has not formed, admixture of sodium carbonate solution leads to the formation of an emulsion. By one to two hours action of the juice, all the oil is hydrolysed with formation of fatty acid and glycerol. Other fats, except castor oil, which is indigestible, are similarly acted on.

Bile alone does not hydrolyse fats, but it considerably hastens the hydrolytic power of pancreatic juice. The following conclusions state some further general results obtained:—

1. Pancreatic juice alone will do a certain piece of work in x minutes; namely, develope in neutral olive oil a sufficient quantity of fatty acid to give the best spontaneous emulsion.

2. The juice in the presence of five parts of 0·25 sodium carbonate solution will require $8x$ minutes to do the same work, and the presence of ten parts of the solution will destroy the action.

3. The juice in the presence of an equal amount of 0·25 per cent. hydrochloric acid will require $3x/2$ minutes to do the same work.

4. The juice in the presence of an equal amount of a mixture of bile and 0·25 per cent. hydrochloric acid will require only $x/4$ minutes to do the work.

The last-mentioned condition is considered analogous to the natural condition of things in the intestine, and thus it appears that the most favourable circumstances are present in the intestine for the carrying out of fat digestion. W. D. H.

Digestion of Gelatin. By R. H. Chittenden and F. P. Solley (*J. Physiol.*, **12**, 23—33).—The investigation of the products of digestion of gelatin were carried out on the same lines as the researches of Kühne, Chittenden, and their pupils on the digestion products of other proteïd and albuminoïd substances.

The following elementary analyses may be first given:—

	Gelatin.	Gastric digestion.		Pancreatic digestion.	
		Proto-gelatose.	Deutero-gelatose.	Proto-gelatose.	Deutero-gelatose.
C	49·38	49·98	49·23	49·45	49·07
H	6·81	6·78	6·84	6·61	6·66
N	17·97	17·86	17·40	17·81	17·52
S	0·71	0·52	0·51	0·57	0·65
O	25·13	24·86	26·02	25·56	26·10
Ash	1·26	1·98	1·08	1·75	1·08

There is thus no marked difference between gelatin and the gelatoses in composition.

Three distinct products are formed from gelatin during digestion; two of these are primary, and are formed both in gastric and pancreatic digestion; they are distinguished from the third product, gelatin peptone by being precipitated by saturation with ammonium sulphate. The proto-gelatose is converted into deutero-gelatose by further ferment action and ultimately into peptone. Proto-gelatose differs from deutero-gelatose by being partially precipitated by saturating its neutral solution with sodium chloride, and completely precipitated by the addition of a little acetic acid to the saturated fluid. Further, proto-gelatose yields a heavy precipitate with hydrogen platinochloride; while deutero-gelatose is not precipitated by these reagents. No trace of a hetero-gelatose was found.

The gelatoses are readily soluble in cold water, and are slowly diffusible. They are undoubtedly formed by hydration, although their chemical composition affords no evidence of this view.

W. D. H.

Myosin-peptone. By R. H. CHITTENDEN and R. GOODWIN (*J. Physiol.*, **12**, 34—40).—This research, carried out on the same lines as the preceding, was more particularly directed to ascertaining the composition and reactions of the final product in the digestion of myosin. The following are the averages of the elementary analyses of the substances in question obtained in this and previous communications :—

	C.	H.	N.	S.	O.
Myosin	52·79	7·12	16·86	1·26	21·97
Proto-myosinose	52·43	7·17	16·92	1·32	22·16
Deutero-myosinose ...	50·79	7·42	17·00	1·22	23·39
Myosin-peptone......	49·26	6·87	16·62	1·16	26·09

In myosin-peptone is seen another instance of the fact that peptones differ from the mother proteïd in containing a lower percentage of carbon, which supports the view that the formation of peptone is the result of hydrolysis.

In reactions myosin-peptone does not differ materially from other peptones equally free from proteoses, and it is characterised, like these, mainly by lack of precipitation by ordinary reagents. Boiled with potassium hydroxide and lead acetate, an aqueous solution becomes darker in colour, but there is no pronounced separation of lead sulphide. Boiled with concentrated hydrochloric acid, there is a noticeable darkening of the fluid. Millon's reagent gives a heavy, white precipitate which, on boiling, becomes dirty yellow, then reddish, whilst the liquid has a dirty red appearance. W. D. H.

Influence of Alkalis on the Secretion and Composition of Bile. By W. NISSEN (*Chem. Centr.*, 1891, i, 335—336).—The bile was collected from a dog with a biliary fistula; the pigment in it was estimated spectrophotometrically, and the bile salts were precipitated and estimated in portions of the bile collected at intervals of a few hours. The administration of 500 c.c. of water caused no difference in its composition. Various alkaline salts (sodium hydrogen carbonate, sodium chloride, potassium acetate, magnesium sulphate, sodium salicylate, &c.) dissolved in the same amount of water also produced no change if the solution was dilute, but lessened the amount of bile when the solution was strong. This appears to be due merely to a diminution of water, the pigment and salts being unchanged in amount; more water is passed from the body by the kidneys.

After the administration of bile or bile salts by the mouth, the amount of bile and of bile acids in the bile is increased, the pigment being unchanged in amount. The increase of water is due to the liver cells being stimulated by the bile acids; the increase in bile acids in the bile is proportional to the amount absorbed by the alimentary canal. W. D. H.

Caseïnogen. By S. Ringer (*J. Physiol.*, **12**, 164—169).—By means of pure rennet and caseïnogen with the addition of calcium chloride, caseïn is formed; thus phosphoric acid is not absolutely necessary for efficient rennet action. Sodium hydrogen carbonate antagonises the action of rennet and calcium chloride. This is not due to the conversion of caseïnogen into alkali-albumin, for if the caseïnogen be precipitated, and dissolved in a solution containing no sodium hydrogen carbonate, it once more is able to clot with rennet and calcium chloride. The clotting of milk by rennet consists of two processes; first, the conversion of caseïnogen into caseïn by rennet; and, secondly, the union of the latter with a lime salt, leading to its precipitation. The calcium chloride used also favours the aggregation of minute particles into masses (curds). The two processes can be separated as follows:—Caseïnogen solution with calcium chloride alone does not clot; with rennet alone it does not clot; but the caseïnogen is nevertheless changed into caseïn, as, after heating to 40° to destroy the rennet, the addition of calcium chloride then causes curdling. W. D. H.

Proteïds of Milk. By J. Sebelien (*J. Physiol.*, **12**, 95—96).—The author reaffirms his statement that milk contains a globulin. This was questioned by Halliburton (this vol., p. 339).

W. D. H.

Chemistry of Sheeps' Milk Cheese. By G. Sartori (*Bied. Centr.*, **20**, 194—196; from *Milchzeit.*, **19**, 1001—1004).—Samples of milk from sheep of the district Agro Romano, on the Tiber, were analysed. The following table (next page) shows the percentage composition of milk collected:—(1) April 1, evening; (2) April 2, evening; (3) January 31, evening; and (4) January 30, morning. The first two were in 1887, the last two in 1890.

The difficulties of separating the cream of sheeps' milk and the peculiar taste of the butter are the chief reasons against the manu-

	Amount in litres.	Sp. gr. at 15°.	Water.	Fat.	Proteïds.	Ash.	Milk-sugar.
1....	405	1·0381	78·37	8·99	6·55	1·04	5·08
2....	390	1·0374	79·04	8·90	6·16	0·99	5·04
3....	338	1·0381*	77·27	10·38	6·28	1·09	—
4....	319	1·0379	77·92	10·04	6·22	0·89	—

facture of sheeps' milk butter in Agro Romano. Bezana, however, succeeded in making butter which did not differ from cows' butter. He was also able to overcome the difficulties in making cheese, and obtained a product very similar to Parmesan cheese. The following analyses are given of cheese prepared from sheeps' milk; 2 and 3 were prepared by the new method, 1, 4, and 5 by the old method:—

	1.	2.	3.	4.	5.
Water	28·50	27·47	29·70	29·13	32·90
Fat	30·93	30·50	31·30	30·30	29·96
Nitrogenous matter	34·19	35·59	33·69	34·00	30·74
KCl	5·03	5·39	4·34	5·51	4·58
Ash (without $NaCl$)	1·35	1·05	0·97	1·33	1·82
Proteïds	27·95	31·57	28·12	28·93	24·63
,, decomposition products	5·94	4·00	5·27	4·86	6·08
Nucleïn	0·261	0·183	0·162	0·256	0·201
Ammonia	0·491	0·162	0·169	0·152	0·143
Total nitrogen	4·83	5·26	4·72	4·70	4·30
Proteïd nitrogen	4·27	4·84	4·28	4·40	3·76
Nitrogen of decomposition products	0·54	0·42	0·41	0·25	0·54
Nitrogen of ammonia	0·157	0·150	0·138	0·125	0·117
Free fatty acids	0·95	1·00	0·85	0·73	0·84

"Ricotta" prepared from sheeps' milk contains more fat and less proteïds than that prepared from cows' milk. The following numbers show the percentage composition of ricotta from the two sources. The results relating to the sheeps' milk ricotta (I) are the mean of those obtained from three samples.

		Water.	Fat.	Proteïds.	Milk-sugar.	Lactic acid.	Ash.
In fresh	I.	43·27	33·31	11·73	10·42	0·43	0·81
	II.	68·47	5·22	18·72	3·97	—	3·62
In dry..	I.	—	58·76	20·66	18·37	0·76	1·43
	II.	—	16·56	59·37	12·59	—	11·48

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* 1·381 is given in Biedermann; the mean of 3 and 4 is given as 1·039.

N. H. M.

Proteoses and Peptones. By R. H. Chittenden and J. A. Hartwell (*J. Physiol.*, **12**, 12—22).—From quantitative experiments on artificial gastric digestion, it was found that the primary proteoses (proto- and hetero-) are only slowly converted into peptone, since they pass through the intermediate stage of deutero-proteose. Deutero-proteose, on the other hand, standing next to peptone, is far more quickly and readily changed, as is shown by the large percentage of peptone formed under the same circumstances as obtained in the digestion of the other proteoses.

The formation of peptone is thus a gradual process, as the greater part of the peptone formed by the action of pepsin-hydrochloric acid passes through the proteose stage, and at the end of the most vigorous gastric digestion a considerable part of the proteïd digested will be in the form of proteose. To how great an extent it will be necessary to modify these conclusions in applying them to the proteolytic changes of natural digestion it is not at present possible to say.

W. D. H.

Peptonised Foods. By P. Horton-Smith (*J. Physiol.*, **12**, 42—71).—"Benger's peptonised beef jelly," "Darby's fluid meat," and peptonised milk prepared by means of Benger's *liquor pancreaticus* in the usual clinical way were analysed as regards their proteïd constituents, and some rough quantitative experiments made as to the relative amounts of proteoses and peptones in them. The results obtained with milk were as follows:—

Neutralisation precipitate......	0·0636	per cent.
Proteose precipitate	1·3900	,,
Peptone	0·3089	,,
Total	1·7625	,,

These results, even allowing for loss due to the formation of amido-acids, are probably too low. They, however, show that the proteïd in the so-called peptonised foods really consists for the most part of proteoses, though containing only a variable amount of true peptone. They cannot, therefore, entirely relieve the digestive organs from work.

The author, having noticed that an old man with liver cirrhosis passed abundance of uric acid when fed on peptonised foods, undertook on his own person to control this observation, but it was found that here the ingestion of large quantities of proteoses and peptones did not disarrange the metabolism of the normal body in the least; perfect health was maintained, the output of uric acid was normal, and its relation to urea unchanged. W. D. H.

Intravascular Coagulation. By A. E. Wright (*J. Physiol.*, **12**, 184—191).—The injection of a solution of Wooldridge's tissue fibrinogen into the veins of a living dog leads to thrombosis of the portal area. During active digestion, clots are also found in the right heart and pulmonary artery. Wooldridge considered that the material in the liver area absorbed from the alimentary tract that favoured coagulation would, during digestion, overflow into the cardiac blood. This, however, cannot be, because coagulation in the portal area can be made to occur after six days inanition, and the injection of tissue fibrinogen leads to universal thrombosis if the animal be made dyspnœic. In the present research, increased venosity of the blood was produced by various methods, asphyxia, muscle tetanus, and retinal stimulation, and, wherever and however caused, subsequent injection of Wooldridge's fluid always led to thrombosis in the area affected. This must be due either to excess of carbonic anhydride or to diminution of oxygen. Animals allowed to breathe air containing a normal amount of oxygen, but excess of carbonic anhydride, suffered from universal thrombosis when the fluid was injected. Thus, increase of carbonic anhydride will alone explain the phenomena. The influence of food, especially of fatty food, as observed by Wooldridge, is probably due to an increased formation of this gas.

W. D. H.

Action of Salts on Heat Coagulation. By S. RINGER and H. SAINSBURY (*J. Physiol.*, **12**, 170—183).—Calcium salts favour the heat coagulation of the proteïds of serum. Magnesium sulphate acts similarly. Zinc salts do not act so. It is of interest to note that, in heat coagulation, as in blood-clotting and rennet action, lime plays an important part. One is led to infer a possible likeness in nature between the heat coagulation and the ferment coagulation of proteïds. One difference, however, is that in heat coagulation the solution becomes more alkaline, whereas in many ferment actions, as in *rigor mortis*, there is development of acid.

Potassium and sodium salts antagonise, to some extent, the favouring action of calcium salts on heat coagulation, as in processes of clotting brought about by ferments, with this difference, however, that sodium and potassium chloride, when used singly, have a slight favouring action in the separation of proteïds by heat.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Sugars present in Fungi. By R. FERRY (*Chem. Centr.*, 1891, i, 220).—An examination of 82 varieties of fungi (*Ascomycetes* and *Basidiomycetes*) showed the very wide distribution of mannitol in these plants; trehalose was found much less frequently. In only a few was there any substance present capable of reducing alkaline copper solution. Several species contained considerable quantities of potassium chloride.

J. W. L.

Composition of the Leaves of Maclura Aurantiaca. By A. PIZZI (*Staz. Sper. Agrar.*, **18**, 589—596).—The leaves of *Maclura aurantiaca*, an American plant, are recommended as a substitute for mulberry leaves for feeding silk-worms. The following analytical results were obtained with leaves of plants grown in Italy, and collected at the end of July. The numbers show the percentage in the fresh leaves:—

Water.	Fat.	Proteïds.	Non-proteïd nitrogenous matter.	Crude cellulose.	Carbo-hydrates.	Ash.
65·71	0·64	4·78	3·23	9·52	12·68	3·42

The ash has the following percentage composition:—

K_2O.	Na_2O.	MgO.	CaO.	Fe_2O_3.	SiO_2.	P_2O_5.	SO_3.	Cl.	Not determined and lost.
9·24	6·16	6·73	25·73	3·81	26·25	17·54	2·41	1·33	1·81

The results are compared with those obtained by others with mulberry leaves grown in Italy and elsewhere, and the composition of the leaves of both plants shows them to be analogous.

With regard to the digestibility of the leaves, the results of experiments with gastric juice show that in 100 parts of dry leaves there is 1·10 parts of nitrogen digested and 1·14 parts not digested, corresponding with 6·85 and 7·03 parts of proteïds respectively. The rest of the nitrogen (1·51 per cent.) is present as amides.

N. H. M.

Chemical Composition and Anatomical Structure of the Fruit of Tomatoes (Lycopersicum esculent.). By G. Brissi and T. Gigli (*Staz. Sper. Agrar.*, **18**, 5—34).—The ripe fruit of tomatoes was separated into skin, seeds, and pulp. The pulp was further separated, by filtration through calico, into a red, insoluble substance and a yellow liquid, both of which were examined qualitatively, and then the various constituents determined quantitatively. The results given below are the averages of several analyses.

The pulp itself forms 85·4 per cent. of the whole fruit; it contains: total dry matter, 4·725; soluble substance, 3·735; and insoluble matter, 1·093 per cent.

The following numbers show the percentage composition (I) of the dry matter of the red insoluble substance, and (II) of the dry matter of the yellow filtrate:—

	I.	II.
Total nitrogen	4·002	2·254
Proteïds	25·012	2·43
Colouring matters	21·128	—
Cellulose	34·390	—
Ash	7·959	10·96
Levulose	—	46·68
Citric acid	—	14·03
Amide-nitrogen	—	0·641
Amido-acid nitrogen	—	1·224

The percentage composition of the ash of the two products is as follows:—

	K_2O.	Na_2O.	CaO.	MgO.	Cl.	SO_3.	P_2O_5.	CO_2.	SiO_2.	Not determined.
I.	—	—	18·127	1·423	—	—	15·866	—	—	64·584
II.	58·554	1·425	1·315	0·169	8·842	0·781	7·182	18·832	0·451	2·449

N. H. M.

Composition of the Fruit of Tomatoes (Solanum lycopersicum). By N. Passerini (*Staz. Sper. Agrar.*, **18**, 545—572; compare preceding abstract).—The fresh fruit of tomatoes consists of skin (1·3), pulp and juice (96·2), and seeds (2·5 per cent.). The pulp contains two colouring matters, a yellow, amorphous substance and a red, crystalline substance. They are both insoluble in water, soluble in amyl alcohol, and very soluble in ether, and both are decolorised by chlorine- and bromine-water. The red crystals are almost insoluble in cold alcohol, whilst the yellow compound is very soluble. Hydrochloric acid has no action on either compound.

The sap of the fruit has a sp. gr. = 0·01833 at 15°, and is lævorotatory. It contains a yellow colouring matter, which differs from that of the pulp in being soluble in water, insoluble in alcohol, ether, chloroform, and light petroleum, and in not being decolorised by chlorine-water or bromine-water. The acidity of the sap is due chiefly to citric acid; it contains also a small amount of an alkaloïd, which, like the acid, decreases as the fruit ripens.

The following table shows the percentage of dry matter (1) in the skins, (2) in the pulp, (3) in the sap, and (4) in the seeds, as well as the percentage composition of the dry matter in each case.

	Dry matter.	Organic matter.	Ash.	Proteïds.	Carbohydrates and fat.
Skins	40·50	99·20	0·80	1·85	97·05
Pulp	6·35	89·56	10·44	15·15	74·41
Sap	2·44	74·52	25·48	21·80	52·72
Seeds.........	53·70	95·56	4·40	25·40	70·16

The carbohydrates of the skins are chiefly in the form of cellulose. The numbers in the last column for sap refer to carbohydrates and acids.

The following analyses are given of the entire fruit collected (1) in September, 1888, and (2) August, 1889; (1) was unripe, and (2) ripe. The percentage of dry matter was 93·50 and 91·01 respectively. The numbers show the percentage in the fruit dried at 105°.

	Glucose.	Citric acid.	Proteïds.	Fat and colouring matter.	Cellulose.	Ash.
1.	2·68	48·53*	11·25	11·73	7·83	8·05
2.	41·54	9·07	11·48	7·02	18·14	12·73

* Citric acid and substances not determined.

The ash of the fruit has the following percentage composition:—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	P_2O_5.	SO_3.	SiO_2.	Cl.
59·46	5·99	1·34	3·09	0·22	12·93	3·49	0·27	19·14

Having regard to the large amount of potash in the fruit, and the large amount of lime in the stems and leaves (the crude ash of the stems contains 28·32 per cent. of lime) the following manuring is recommended for tomatoes:—Farmyard manure, 5000 kilos., calcium superphosphate (18 per cent.), 30 kilos.; potassium chloride (50 per cent.), 60 kilos. per hectare. N. H. M.

The Non-nitrogenous Extract-substance from Barley, Malt, and Beer. By C. J. LINTNER (*Bied. Centr.*, **20**, 198—200; from *Allgem. Brauer- u. Hopfenzeit*, 1890, No. 128).—When beer is shaken violently with ether, an emulsion is obtained which, only after a long time, separates into two layers. The ethereal layer contains a slimy mass in suspension, like frog's spawn. This substance, which is occasioned by the presence of gummy substance, can be obtained from barley, malt, or beer, in the following manner:—Barley or malt (1 part) is digested with water (5 parts) for a day at the ordinary temperature, filtered, washed, and concentrated by evaporation. It is again filtered and treated with absolute alcohol, as long as a precipitate is formed. This precipitate is filtered by suction, washed with ether, dried, and dissolved in water, with addition of potash. It is filtered, and the filtrate treated with aqueous copper sulphate, being stirred at the same time; a precipitate, the copper oxide compound of the gum, is formed and quickly settles. It is of importance that the liquid should remain strongly alkaline. The precipitate is washed by decantation, until no longer alkaline, filtered, dissolved in strong hydrochloric acid, and precipitated by alcohol: as the first precipitate still contains some copper, this is repeated twice. It is filtered, washed with alcohol, and finally with ether, dried in a vacuum over sulphuric acid, and then at 110° It is thus obtained as a pure white, very loose powder. When dried in air, it is vitreous and transparent. Both modifications are non-hygroscopic, and dissolve slowly in cold water, but without giving a quite clear solution. It is lævorotatory; after treatment with dilute acids, it is dextrorotatory. It contains carbon (40·00 per cent.) and hydrogen (6·66 per cent.) corresponding with the formula of arabinose, $C_5H_{10}O_5$; some reactions indicate that it is a substance with 5 (or a multiple of 5) carbon atoms.

It is obtained from beer as described above; Munich beer yielded 0·25 per cent. N. H. M.

Constituents of the Fruit and Seed of Illicium anisatum. By F. OSWALD (*Arch. Pharm.* [2], **29**, 84—115).—The fruit of the Staranise extracted with light petroleum yields a mixture of ethereal and fatty oils. The former oil consists essentially of anethoïl. It contains, also, small quantities of terpenes, safrole, quinol ethyl ether, anisic acid, and probably other aromatic compounds which, by oxidation, give rise, amongst other compounds, to veratric acid and piperonal. The fatty oil contains considerable amounts of fatty and oleïc glycerides, with detectable amounts of cholesterol and phosphates. The aqueous extract contains protocatechuic acid, and shikimic acid, discovered by Eijkman. Sugar is not present in the fruit of this plant in any considerable quantity; its sweet taste is to be ascribed essentially to the presence of the ethereal oil. No nitrogenous bases could be detected in the aqueous extract. J. T.

Soil containing Iron and Chromium from the Andaman Islands, East Indies. By C. J. H. WARDEN (*Chem. News*, **63**, 85).—These islands are remarkable for the great diversity of soil found on them. The one in question, a rich loamy soil, came from a coffee plantation, and has been submitted to mechanical analysis and various physical tests by the author, the results of which are detailed in the paper; the numbers from chemical analysis in percentages of air-dry soil are as follows:—

Loss at 100°		11·3410
Loss on ignition	water	2·2773
	organic matter	10·4459
	nitric nitrogen	0·00129
	organic and ammoniacal nitrogen	0·24080

Soluble in water and concentrated hydrochloric acid:—CaO, 0·294; Fe_2O_3, 35·433; Al_2O_3, 10·491; MgO, 0·109; Cr_2O_3, trace; Mn_3O_4, 0·417; Na_2O, 0·455; K_2O, 0·863: Cl, 0·006; P_2O_5, 0·401; SO_3, 0·139; CO_2, trace; SiO_2, 0·046. Insoluble portions:—soluble in alkalis, 14·4819 per cent.; not dissolved by alkalis, but decomposed by sulphuric acid, 2·6569 per cent., containing Fe_2O_3, Al_2O_3, Cr_2O_3 = 2·425; not decomposed by sulphuric acid, 9·256 per cent. The total amount of Cr_2O_3 present was 1·6139 per cent. D. A. L.

Soil Analyses. By A. MAYER (*Bied. Centr.*, **20**, 149—151; from *J. f. Landw.*, **38**, 157—163).—In connection with the project for reclaiming land between Friesland and Ameland, a large number of mud samples were examined. When the samples are arranged according to the percentage of sand they contain, they show a certain regularity of composition as regards some important constituents (besides clay). The same inverse proportion is shown between sand and humus and between sand and hygroscopic moisture of the air-dried soils. The following numerical results are given:—

Soil sample.	Clay.	Humus.	Moisture.
90—100 p. c. of sand..	0·0— 4·8	0·2— 2·4	0·0— 0·5
60—80 ,, ..	5·6—24·1	1·1— 6·6	0·3— 2·9
20—40 ,, ..	34·2—55·8	5·6—14·4	2·6—10·6

The variation in the amount of chalk showed no regularity, but this was of no great practical importance, as all the samples contained more than sufficient chalk. The amount of phosphoric acid was always in exact relation to the clay. Thus, samples with 90 per cent.

of sand contained 0·04 per cent., with 30 per cent. of sand 0·15 per cent. of phosphoric acid soluble in nitric acid. The amount of sand was always an excellent measure of the fertility of the soil.

The method employed was that already described by the author (*Lehrb. d. Agr. Chem.*, **2**, 53). The soil (10 grams) is treated with dilute hydrochloric acid to remove chalk, and the separation of sand and clay conducted in a Schöne's apparatus so arranged that, at a water pressure of 5 cm., 1 litre flows out in 10 minutes. The sand is ignited and weighed. The amount of clay is ascertained by difference, when, from the original amount, the sand humus and moisture are subtracted. N. H. M.

Analytical Chemistry.

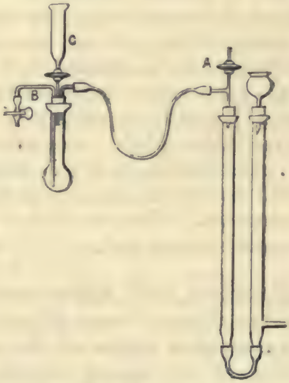
Dry Reactions in Qualitative Analysis. By W. TATE (*Chem. News*, **63**, 86—87).—The author advocates the systematic application of dry reactions in qualitative analysis employing the moist group precipitates, obtained in the ordinary manner, for the purpose; groups II and III being subdivided respectively into the copper and arsenic and the zinc and iron sub-groups. As an example of the proposed method:—Group I precipitate is examined, α, for mercury, by heating a minute quantity on a thread of asbestos in the upper reducing flame of a Bunsen and beneath a cooled porcelain surface, the sublimate being converted into iodide for confirmation; β, for lead, by heating on charcoal until the mercury is dissipated, and heating any residue strongly with potassium iodide and sulphur; γ, for silver, by obtaining bead on charcoal. The method of examining the other groups in a similar manner is described. D. A. L.

Standardising Acidimetric and Alkalimetric Solutions. By E. HART and S. CROASDALE (*Chem. News*, **63**, 93—94; from *J. anal. Chem.*, **4**, part 4).—Advantage is taken of the well-known accuracy of the electrolytic method of estimating copper, and therefore pure copper sulphate is electrolysed, and the copper carefully weighed. The exact amount of sulphuric acid in solution is then readily ascertained, and is employed for standardising any desired alkaline solution, which, in its turn, serves for controlling the standard acids. By this means, various disadvantages attached to the use of sodium carbonate, oxalic acid, or potassium oxalate are obviated.

D. A. L.

The Liquoscope: an Instrument for Comparing the Refractive Indices of Liquids. By K. SONDÉN (*Zeit. anal. Chem.*, **30**, 196—199).—The apparatus consists of two similar hollow prisms, which are immersed, side by side, in a glycerol-bath formed of a cylindrical vessel with glass ends. When both prisms are filled with liquids having the same refractive index, a horizontal black line observed through them appears continuous; but if the indices are different, one part of the line is displaced with respect to the other. The instrument is very serviceable for indicating adulteration of butter, oils, glycerol, &c. M. J. S.

Estimation of Nitric Acid by Reduction to Ammonia. By K. Ulsch (*Zeit. anal. Chem.*, **30**, 175—195).—The reduction of nitric acid to ammonia by iron and sulphuric acid takes places with quantitative completeness (this vol., p. 617).—The estimation can be very conveniently made by means of the deficit in the hydrogen evolved. The iron for this purpose, which should be in the form of the most finely-powdered wrought-iron filings, as free as possible from oxide, should be coated with copper by warming 3 grams of it with 20 c.c. of a 10 per cent. solution of copper sulphate, and washing. This quantity suffices for 25 estimations, when working on about 10 milligrams of nitrate. On warming a known quantity of sulphuric (or hydrochloric) acid with an excess of this couple, a constant volume of hydrogen is evolved, and the reaction is rapidly and sharply completed. The presence of 1 mol. of a nitrate $(M'NO_3)$ causes a deficit of 10 atoms of hydrogen, or 1·106 c.c. of hydrogen (dry, and at 0° and 760 mm.) per milligram of potassium nitrate. The apparatus used is here figured.



The decomposition flask holds about 30 c.c., the azotometer 50 c.c., of gas. The tube B has a diameter of 3 mm., and is used for removing the spent liquids. The narrow tube of C should be drawn to a fine point, and bent towards the wall of the neck of the flask.

Before commencing a series of estimations, the air in the apparatus must be displaced by hydrogen, by adding 10 c.c. of normal sulphuric acid to the iron-copper couple in the flask, and warming to 75° with vigorous shaking, whilst the cock A remains open, and the azotometer is filled to the top with water. This treatment removes traces of iron oxide at the same time. The flask is then cooled in a water-bath to the temperature of the air, the water is adjusted to zero, and the apparatus is ready for use. It is necessary to ascertain the exact volume of hydrogen yielded by 20 c.c. of the N/10 sulphuric acid in use, as this is slightly below theory. By warming to 75°, the reaction is complete in about three minutes. The same volume of acid with the nitrate dissolved in it is then used for the estimation. The temperature of 75° must not be exceeded, since, even at 80°, the couple decomposes water, and an excess of hydrogen would be evolved. (Should this have occurred in any one case, the following experiment, if conducted at a temperature not exceeding 75°, would show an exactly equal deficiency of hydrogen.) The volume of the liquid introduced has to be deducted from the observed volume of gas; the acid in C cannot therefore be rinsed into the flask, but C must be wetted with acid of the same strength as that to be measured into it. A certain excess of acid seems to be necessary, but 20 c.c. of N/10 acid suffices for 15 milligrams of potassium nitrate. The test estimations reported are highly satisfactory, and the method seems to be one of the most rapid known. In the absence of nitrates it may also be used as an acidimetric method. Hydrochloric acid, although it yields precisely the same volume of hydrogen as sulphuric acid, cannot be used in the estimation of nitrates, since low results are always obtained. The presence of much chloride is therefore inadmissible.

M. J. S.

Nitrates in Wine. By M. Zecchini (*Staz. Sper. Agrar.*, **18**, 35—40).—In testing for nitrates in wine by diphenylamine, it is not sufficient to decolorise the wine with animal charcoal or to precipitate with basic lead acetate, as there still remain substances which give a brown colour with sulphuric acid, and so mask the reaction, if any, with diphenylamine. The following method is recommended as being easy to carry out, and not liable to the danger of introducing nitrates:—50 or 100 c.c. of wine, contained in a porcelain capsule, is treated with a slight excess of lime (prepared from marble) and evaporated to dryness. The residue is detached from the sides of the capsule, well stirred with 20 or 30 c.c. of 92—95 per cent. alcohol, left for about 10 minutes, and filtered. The filtrate is evaporated down on a water-bath, and the residue dissolved in a little pure, distilled water (about 1 c.c.). Half of the solution is tested with diphenylamine; if the coloration is very intense, the experiment is repeated two or three times with more dilute solutions. In this manner it is possible to ascertain whether a larger or smaller amount of nitrate is present.

When wine contains much sugar, it may be necessary to repeat the treatment with lime and alcohol; but this is unnecessary in most cases.

N. H. M.

Densimetric Estimation of the Phosphorus in Iron. By E. E. Metz (*Zeit. anal. Chem.*, **30**, 200—206).—The principle introduced by Popper (Abstr., 1877, 638, and 1879, 480) of ascertaining the weight of a precipitate without washing or drying it, by transferring it to a specific gravity bottle, which is filled up with a liquid of known density, and weighing the whole, appeared to be suitable for ammonium phosphomolybdate, owing to the high specific gravity of the precipitate. This was found, as an average of four determinations, to be 3·252. The precipitation took place in a stoppered cylinder of about 250 c.c. capacity, the lower end of which was prolonged into an almost capillary tube of 2 c.c. capacity, with a stop-cock at the bottom. The oxidised solution of the iron (0·5 gram in 50 c.c.) after removal of silica, was introduced into this vessel and mixed, first with 20 c.c. of strong ammonia and subsequently with just enough nitric acid to redissolve the precipitate; then (without allowing to cool) 100 c.c. of molybdate solution at about 60° was added, the whole well shaken, and the precipitate allowed to subside until it had wholly entered the narrow tube. After part of the clear liquid had been poured out and its specific gravity ascertained, then, without rinsing the pyknometer, the precipitate was delivered into it by opening the stop-cock. In six test analyses, of which details are given, the results agree closely enough with those of gravimetric estimations to be employed for technical purposes. M. J. S.

Assaying Lead Ores by Fusion with Potassium Cyanide. By W. J. Cooper (*Chem. News*, **63**, 73).—The author's experiments show that with an ore of the following percentage composition:—SiO_2, 83·05; Fe_2S_3,Cu_2S, 10·639; FeS_2, 2·967; PbS, 3·001; Au, trace; Fe_2O_3, 0·343; the dry cyanide method for the assay of lead ores offers no advantage over the ordinary wet methods. D. A. L.

Assaying Lead Ores by Fusion with Potassium Cyanide. By A. W. Warwick (*Chem. News*, **63**, 145—146).—A continuation of a previous communication (this vol., p. 863). Anglesite and pyromorphite have now been successfully treated, the latter requiring a very high finishing temperature. It is obvious that minerals or ores containing large quantities of other reducible minerals, which will come down with the lead, such as the ore tried by W. J. Cooper (preceding abstract), are not suitable for assaying by the cyanide method.

D. A. L.

Estimation of Mercury in Animal Tissues. By F. Hofmeister (*Zeit. anal. Chem*, **30**, 258—259).—The tissue is minced and heated with its own weight of 20 per cent. hydrochloric acid, in a flask with reflux condenser, until completely dissolved. After cooling to 60°, a few grams of potassium chlorate is added in small portions, and the cooled and filtered liquid is shaken with about 5 grams of zinc-dust, to precipitate the mercury. The precipitate is washed successively with water, with soda, and again with water, collected on glass wool, washed with alcohol, and air-dried. It is then introduced into a combustion tube containing columns of granulated lime and copper oxide between asbestos plugs. One end of the tube is drawn out to a U-shape. The mercury is distilled from the zinc in a stream of dry air, over the red-hot lime and copper oxide into the U-tube, where it condenses.

In examining urine, the destruction of the organic matter should not be attempted. It suffices to gently warm the urine with hydrochloric acid before adding the zinc-dust. M. J. S.

Volumetric Estimation of Manganese. By T. Moore (*Chem. News*, **63**, 66—67).—The following method of estimating manganese is recommended as yielding excellent results:—The material, dissolved in syrupy phosphoric acid (sp. gr. 1·75) or in solution to which that acid has been added, is oxidised by warming gently with potassium chlorate; when all the chlorine has been expelled, the solution is diluted and titrated with ferrous sulphate until the violet colour disappears, or the ferrous sulphate is added in excess and titrated back with permanganate. The equation $Mn_2O_3 + 2FeO = 2MnO + Fe_2O_3$ represents the change, and therefore 1 part of iron is equivalent to 1·4108 of manganic oxide. The only metal which is found to interfere with the method is chromium; however, when cobalt is present it is well to add excess of ferrous sulphate, annul the cobalt colour with nickel sulphate, and then titrate back with permanganate. Nitrites are obviously undesirable; therefore potassium chlorate is preferable to the nitrate for the oxidation. D. A. L.

Quantitative Separation of Manganese and Zinc. By P. JANNASCH and J. F. MACGREGORY (*J. pr. Chem.* [2], **43**, 402—406).—To the hydrochloric acid solution (75—100 c.c.) containing the manganese and zinc in a porcelain dish, are added a 15—20 per cent. solution of ammonium chloride, and then ammonia until the liquid is strongly alkaline; the mixture is stirred and hydrogen peroxide added until oxygen begins to be rapidly evolved; the dish is then heated on the water-bath for 10—15 minutes, the precipitated manganese dioxide filtered, washed, first with hot ammonia water, then with hot pure water, and ignited whilst still moist in a platinum or porcelain crucible, being finally heated over the blowpipe until constant in weight. The zinc may be precipitated from the mixed filtrate and washings with ammonium sulphide, but is more rapidly determined by evaporating to dryness in a platinum dish, heating the residue first at 125—150° for one hour and then over a flame, with an intervening asbestos millboard to prevent too high a temperature and consequent loss of zinc; the residue is dissolved in hot water with a drop or two of hydrochloric acid, and the solution precipitated with hot sodium carbonate solution. A. G. B.

Estimation of Manganese in Iron and Steel. By L. BLUM (*Zeit. anal. Chem.*, **30**, 210—211).—The modification of Volhard's process proposed by Rürup contains several sources of error. The method consists in dissolving and oxidising 6 grams of substance, neutralising, and adding sodium sulphate, making up to a litre, and filtering. Of the filtrate, 500 c.c. is mixed with zinc oxide, heated, and titrated with potassium permanganate. According to Meineke, however, the presence of free zinc oxide and the absence of soluble zinc salts are both conditions leading to low results. On the other hand, the neglect of the bulk of the basic ferric sulphate has an opposite influence. The advantage of the method would in any case be small, since an estimation by Volhard's process can be completed within an hour. M. J. S.

Glaser's Method for the Estimation of Ferric Oxide and Alumina in Phosphates. By v. GRUBER (*Zeit. anal. Chem.*, **30**, 206—207; see this vol., p. 501).—The modifications introduced into this process by Jones are acknowledged to be improvements. Jones dissolves 5 grams of substance to 500 c.c.; takes 100 c.c. and evaporates it to about half, adds 10 c.c. of dilute sulphuric acid (1 : 5), and then 150 c.c. of alcohol. After a repose of three hours, the precipitate is filtered off and washed with alcohol until neutral. In precipitating the earthy phosphates, the complete expulsion of the excess of ammonia is essential; the precipitate would otherwise contain magnesia. M. J. S.

Tannin in Urine. By S. KATHREIN (*Chem. Centr.*, 1891, i, 272—273; *Pharm. Zeit.*, **35**, 785).—The author recommends the following test:—4—5 c.c. of urine, either after remaining a short time or warmed, is mixed with 5—10 drops of iodine solution (1 : 10); the urine is shaken after the addition of each drop of iodine. In the presence of tannin, a beautiful and characteristic green coloration is produced; with excess of iodine, the coloration becomes brownish-red. In the absence of tannin, the iodine is at first absorbed, and then a red coloration is produced, which changes to reddish-brown on the addition of more iodine. J. W. L.

Fractional Crystallisation of Quinine Sulphate. By L. PRUNIER (*J. Pharm.* [5], **23**, 265—270 and 387—390).—A quinine sulphate containing 6 per cent. of foreign sulphate, when saturated at 100°, gives scarcely any deposit on cooling to 90°; from 90° to 50°, the crystals have nearly a constant composition and contain not more than 1 to 2 per cent. of impurity. Below 50° (and principally about 40°), more than the average amount of cinchonidine appears in the deposit. Between 35° and 25° usually, an abundant crystallisation takes place, dependent on the proportion of cinchonidine and cinchonine present with the quinine; this arises from the separation in a solid form of molecular compounds, and sufficient time is required before filtering off the liquid which is to be employed for the ammonia assay of the quinine sulphate. The results with various samples of sulphate show that the amount of aqueous ammonia required in the ammonia test diminishes with the temperature of filtration. An inspection of the curves plotted from these results shows that the temperature 15°, selected for filtration in the ammonia assay, has been well chosen. J. T.

Estimation of Theïne in Tea. By G. L. SPENCER (*Chem. Centr.*, 1891, i, 373; from *J. Anal. Chem.*, **4**, pt. 4).—3 grams of the tea is boiled for half an hour in a 300 c.c. flask, cooled, and a slight excess of lead acetate added (about 0·3 c.c. of concentrated solution per 1 gram of tea). The flask is filled to the mark, shaken, and filtered. 100 c.c. of the filtrate is precipitated with hydrogen sulphide in a flask graduated at 100 c.c. and 110 c.c. The conducting tube is washed with 10 c.c. of water, filtered, and 55 c.c. of the filtrate is extracted seven times with chloroform. The chloroform is evaporated, and the residue, dried at a temperature not exceeding 79°, represents the theïne from 0·5 gram of tea. J. W. L.

General and Physical Chemistry.

Spectra of the Elements of the Second Periodic Group. By H. Kayser and C. Runge (*Ann. Phys. Chem.* [2], **43**, 385—409).—In a former paper (this vol., p. 137), the authors studied the relations of the line spectra of the alkali metals. They now extend their investigation, using the same methods, to the metals of the alkaline earths and the zinc group. The spectrum of beryllium, on account of its poverty in lines, is left out of consideration.

The values of the constants in the formula $A - B_n^{-2} - C_n^{-4}$ for the first lines in each series of triplets are contained in the following table:—

	First series.			Second series.		
	A.	B.	C.	A.	B.	C.
Mg	39796	130398	1432090	39837	125471	518781
Ca	33919	123547	961696	34041	120398	346097
Sr	31030	122328	837473	—	—	—
Zn	42945	131641	1236125	42955	126919	532850
Cd	40755	128635	1289619	40797	126146	555137
Hg	40159	127484	1252695	40218	126361	613268

Barium gives no series of triplets. It will be seen from the table that the bivalent elements fall into two groups, namely, the alkaline earths and the zinc-mercury group. In each the values of the constants decrease in general with increasing atomic weight.

J. W.

Chemical Effects of Light: Measurement of Physical Absorption. By G. Lemoine (*Compt. rend.*, **112**, 936—938).—The experiments were made with a solution of ferric chloride and oxalic acid, the quantity of ferrous salt formed being estimated. One cell containing this solution was exposed directly to light, whilst a similar cell was exposed behind the medium the absorption of which was under investigation. In the case of ferric chloride, the absorption varies somewhat with the state of the atmosphere, but under favourable conditions the variations are not great, and the results may be represented by the following expression, which is calculated for semi-normal ferric chloride, i being the intensity of the transmitted light, and l the thickness of the absorbing layer, $i = 0{\cdot}01(0986)^l + 0{\cdot}07(0{\cdot}40)^l + 0{\cdot}13(0{\cdot}10)^l + 0{\cdot}79(10^{-10})^l$.

C. H. B.

Determination of the Maximum Conductivity of Very Dilute Copper Sulphate Solutions. By P. Sack (*Ann. Phys.*

Chem. [2], **43**, 212—224).—As a deduction from the dissociation hypothesis, Arrhenius has shown that the conductivity of electrolytes must reach a maximum as the temperature increases, and then begin to fall (Abstr., 1889, 1044). Experimental confirmation of the theoretical conclusions was obtained for the cases of hypophosphorous and phosphoric acids, but owing to the difficulty of determining the conductivity at high temperatures, no further confirmation has, up to the present, been obtained. The author has, however, succeeded in determining the conductivity of dilute copper sulphate solutions at temperatures up to 120°, the solutions being contained in a sealed apparatus to prevent change of concentration by evaporation. Measurements were thus successfully obtained for three solutions of 0·327 per cent., 0·5 per cent., and 0·64 per cent. concentration, and in each case the conductivity was observed to reach a maximum: for the first solution at 94°, for the second at 95°, and for the third at 96°. A calculation of the temperature of maximum conductivity for the third solution by means of the formula given by Arrhenius (*loc. cit.*) gave 99°. H. C.

Thermochemistry of Platinic Chloride and its Compounds. By L. Pigeon (*Compt. rend.*, **112**, 791—793).—The heat of dissolution of anhydrous platinic chloride, $PtCl_4$, is +19·58 Cal.; hence $Pt + Cl_4 + Aq = PtCl_4$ diss. develops +79·40 Cal. (compare Abstr., 1890, 439). The last value has been verified by reducing a solution of platinic chloride with cobalt, the number obtained being +79·66 Cal. The heat of dissolution of the hydrate $PtCl_4 + 4H_2O$ is −1·74 Cal., and hence $PtCl_4$ sol. + $4H_2O$ liq. = $PtCl_4,4H_2O$ sol. develops +21·32 Cal. The reduction of solutions of the alkaline platinochlorides by metallic cobalt shows that

$Pt + Cl_4 + 2NaCl$ diss. $= Na_2PtCl_6$ diss. develops +85·09 Cal.
$Pt + Cl_4 + 2KCl$ diss. $= K_2PtCl_6$ diss... ,, +83·33 ,,

hence,

$PtCl_4 + 2NaCl$ diss. $= Na_2PtCl_6$ diss. ... ,, +25·29 ,,
$PtCl_4 + 2KCl$ diss. $= K_2PtCl_6$ diss. .... ,, +23·53 ,,

$PtCl_4 + 2HCl$ diss. $= H_2PtCl_6$ diss. .... ,, +24·8 ,,

In the preparation of hydrated platinic chloride by Norton's method, the liquid is at first colourless, and is free from both silver and platinum, but contains a yellow precipitate which must be regarded as silver platinochloride. After some time, especially if heated, the precipitate gradually becomes white, whilst the colour of the liquid becomes deeper. Direct experiment shows that the union of platinic chloride with silver chloride would develop +7·42 Cal., a number considerably lower than the heat of combination of platinic chloride with water, so that

$Ag_2PtCl_6 + Aq = PtCl_4.Aq + 2AgCl$ develops + 12·16 Cal.

C. H. B.

Calorimetric Data. By BERTHELOT (*Compt. rend.*, **112**, 829—834). —*Aspartic Acid.*—Heat of dissolution at 16° −7·25 Cal., heat of neutralisation by sodium hydroxide, first equivalent +3·0 Cal., second equivalent +3·5 Cal., third equivalent 0·0 Cal. In concentrated solution the second equivalent of alkali develops +3·9 Cal. The second acidic function of aspartic acid, as in the case of many allied acids, is not equivalent to the first.

Malonic Chloride, $CH_2(COCl)_2$.—Decomposition by excess of water develops +44·5 Cal.; decomposition by excess of sodium hydroxide develops +99·7 Cal. The heat developed by the action of water on a molecule of malonic chloride is practically double that developed by the similar decomposition of a molecule of acetic chloride (+23·3 Cal.). The corresponding value for butyric chloride is +21·7 Cal. (Louguinine).

$CH_2(COCl)_2$ liq. + $2H_2O$ liq. = $C_3H_4O_4$
cryst. + 2HCl gas .... develops +14·2 Cal.

Tartrates.—When normal sodium dextrotartrate is mixed with calcium chloride, there is development of heat but no precipitation. After a few minutes, a precipitate separates with a further and greater development of heat, the values being for 1 mol. of the salt +0·98 Cal. and +2·68 Cal. respectively.

Sodium lævotartrate behaves in a similar manner, the values being respectively +0·92 Cal. and +2·60 Cal.

Sodium paratartrate is formed without thermal disturbance by mixing equal quantities of the dextro- and lævo-tartrates. When an equivalent quantity of calcium chloride is added, precipitation begins at once, and the thermal disturbance, which at first is equal to +2·20 Cal., rises after a few minutes to +6·3 Cal., the development of heat being perfectly continuous from the moment of mixing up to the maximum.

The heats of neutralisation of the four tartaric acids by sodium hydroxide are practically identical under similar conditions of temperature and concentration, the heat developed being +12·7 Cal. per equivalent.

A solution of sodium paratartrate made by neutralisation of paratartaric acid, and mixed immediately with calcium chloride, gives precisely the same thermal disturbance as the solution obtained by mixing the lævo- and dextro-tartrates. The sodium salt of the true inactive tartaric acid under the same conditions yields a precipitate of an insoluble calcium salt with the development of only +3·0 Cal.

Sodium lævo- and dextro-tartrates, when precipitated with an equivalent quantity of silver nitrate, give a continuous development of heat rising from +1·5 Cal. to a total of +4·6 Cal. in the first case, and from +1·1 Cal. to a total of +4·5 Cal. in the second case. Sodium paratartrate, or a mixture of the lævo- and dextro-tartrates, gives an immediate precipitate with a total development of +5·7 Cal.

The greater heat of formation of the insoluble paratartrates corresponds with the greater heat of formation of paratartaric acid as established by the author and Jungfleisch. C. H. B.

Thermochemistry of Bibasic Organic Acids. By G. MASSOL (*Compt. rend.*, **112**, 1062—1065).—The author has applied Berthelot's method of calculating the heats of formation of solid salts to the consideration of the relative energy of combination of the first equivalent and the second equivalent respectively of a base with bibasic acids of the oxalic acid type. The heat of neutralisation per equivalent of base of these acids in dilute solution varies from +13 to +14 Cal. In the cases of oxalic and malonic acids, and also with sulphuric, arsenious, and selenic acids, the second equivalent of base disengages rather more heat than the first; whereas succinic, tartaric, sulphurous, selenious, and arsenic acids set free more heat with the first equivalent. The differences vary between 0·5 Cal. and 1 Cal. For the solid salts, the heats of formation are as follows :—

Acids :—	Oxalic.	Malonic.	Succinic.	Sulphuric.	
1st KOH....	+34·28	+27·87	+25·26	+47·8	Cal.
2nd KOH ...	+24·69	+20·70	+21·15	+33·6	„
Total ...	+58·97	+48·57	+46·40	+81·4	„
1st NaOH ..	+28·3	+25·8	—	+42·7	Cal.
2nd NaOH ..	+24·7	+15·6	—	+26·6	„
Total ...	+53·0	+41·4	+40·0	+69·3	„

Hence it is evident that in reality the addition of the first equivalent of a base to a bibasic acid with formation of the acid salt sets free more heat than the addition of the second equivalent to form the normal salt. The author thinks that these data give no grounds for assuming an unsymmetrical constitution for the acids, but attributes the thermal differences to a reciprocal action between the two acid groups. This point he illustrates from the data given above. Oxalic acid may be viewed as a substituted formic acid; the two COOH groups appear when near together to cause a mutual strengthening of the acid function, and the bibasic oxalic acid has more than double the heat of neutralisation of formic acid, but when one of these groups is neutralised, the acid salt acts just like formic acid, and has almost the same heat of neutralisation. Malonic and succinic acids behave similarly, the COOH groups having less reciprocal action as they become farther apart in the molecule.

Berthelot observes, with respect to the above paper, that it contains new facts relative to the salts of malonic and succinic acids, but that the conclusion as to the greater heat liberated by the first equivalent of the base is a necessary consequence of the known fact (*Ann. Chim. Phys.* [5], **4**, 130) that the union of a bibasic acid with its own normal salt to form an acid salt, in the solid state, disengages heat. It is by the difference between the heats of formation of the acid and normal salts that he has explained the reciprocal actions and the equilibrium between a monobasic and a bibasic acid, for instance, the decomposition of normal sulphates by nitric and hydrochloric acids (*Essai de Mec. Chim.* [2], 586). W. T.

Thermochemistry of Dextro- and Lævo-tartaric Acids. By H. JAHN (*Ann. Phys. Chem.*, **43**, 306—309).—A solution containing dextrotartaric acid was mixed in a Bunsen's ice-calorimeter with an equally strong solution of lævotartaric acid. No thermal effect was observed. It was also found that the heat of neutralisation of these acids by an optically active base (morphine, nicotine) was the same in both cases. J. W.

Vapour Pressures of Homologous Compounds. By G. C. SCHMIDT (*Zeit. physikal. Chem.*, **7**, 433—468).—Dalton's law that the vapour pressures of all compounds are the same at equal distances from their boiling points has been shown by Regnault and others to be incorrect when applied generally. But it still remains doubtful whether this law does not hold among organic compounds belonging to the same homologous series, although according to the researches of Kahlbaum this is not the case. Examining the evidence for and against, the author found so much discrepancy between the data of different observers, that he decided to submit this point to a very thorough experimental examination. The present paper contains his results with acids of the acetic series, from formic to valeric acid. The substances were heated in a bulb attached to an air-pump and manometer, and the boiling points under different pressures were measured. Great care was taken to ensure the purity of all material used. From the results it is evident that for the compounds examined, and for all pressures below 760 mm., Dalton's law holds with remarkable accuracy. For instance, taking the two extreme cases, the decrease in the boiling point of formic acid with a decrease of pressure from 760 to 10 mm. is 102·8°, and that of valeric acid 103·8°, two numbers which in view of the numerous sources of error may be regarded as identical. The author intends to investigate other homologous series in like manner. H. C.

Data for the Critical State of Liquids. By E. HEILBORN (*Zeit. physikal. Chem.*, **7**, 601—613).—The author has brought together in a series of tables the critical data (temperature, pressure, and volume) of the substances which have been investigated in this direction.

Copious references and annotations are given. J. W.

Adhesion at the Freezing Point. By F. WALD (*Zeit. physikal. Chem.*, **7**, 514—517).—If a liquid wets a solid substance, it follows from thermodynamical considerations that the vapour tension of the liquid will be reduced, and that it will exercise a pressure on the solid. Applying this view to the case of melting ice, if the water first formed remains in contact with and wets the ice, its vapour pressure will be less than that of water at 0°. But since the vapour pressure of the water in contact with the ice is equal to that of the ice itself, the vapour pressure of dry ice should be less than that of water at 0°, and not equal to it, as has been hitherto assumed.

H. C.

Dissociation of Amylene Hydrobromide under Low Pressures. By G. Lemoine (*Compt. rend.*, **112**, 855—858).—The following data were obtained with carefully purified amylene bromide:—

Pressure	764	452	238	121	43	21 mm.
Boiling point ..	105°	90°	71°	55°	34°	28°

Temperature	0·1°	7·2°	18·6°	38°	61°	90°	97°
Sp. gr.	1·224	1·215	1·200	1·176	1·146	1·106	1·100

$$D_t = D_o\,(1 - 0{\cdot}00102t - 0{\cdot}0000004t^2).$$

	52—15°.	58—16°.	87—17°.
Sp. heat	0·324	0·325	0·335

The determinations of the vapour pressures under ordinary atmospheric pressure indicate more decomposition than was observed by Wurtz, a result probably due to the fact that by means of a thermoregulator they were prolonged for several hours, in order to attain the limit of decomposition.

The most striking phenomenon is the great variation in the sp. gr. between 175° and 190°.

	Temperature....	100	150°	175°	185°	200°	225°	300°
1 atmos.	Sp. gr. of vapour	,,	5·2	5·0	4·1	3·5	3·0	2·6
	Proportion decomposed	,,	0	0·05	0·28	0·50	0·75	1
$\frac{1}{10}$ atmos.	Sp. gr of vapour	5·0	4·6	4·1	3·4	3·1	2·8?	2·6
	Proportion decomposed	0·05	0·14	0·28	0·54	0·69	0·87?	1

It is clear that reduction of pressure facilitates decomposition.

C. H. B.

Diffusion of Fresh Water into Sea Water. By J. Thoulet (*Compt. rend.*, **112**, 1068—1070).—A cylindrical vessel of 600 c.c. capacity, divided into parts of equal height and equal capacity, was filled up to the 300 c.c. mark with sea water, concentrated to a density of 1·0646; six small spheres of wax, so weighted with quartz that their densities ranged between the density of the salt water and that of fresh water, were placed on the surface, and 300 c.c. of distilled water added without causing any admixture. The vessel was placed in a cellar, with coverings to protect it from changes of temperature. The positions of the spheres were noted from time to time, and the curve belonging to each traced out. The diffusion was very slow, requiring, according to the indications given in 5 months, about 18 months to become complete. From the consideration of the curves of density the following deductions have been drawn:—The fresh water seems to pass into the saline solution as if its molecules interposed themselves between the molecules of the salt; they travel in such a manner that, at any moment, the quantity of fresh water is the same in each horizontal plane of the liquid; it follows that the elementary speed of diffusion is the same, whatever may be the percentage of salt in the solution.

The velocity of diffusion decreases with the time. The decrease cannot be infinite, for then two different salt solutions would never completely mix. W. T.

Cryoscopy of Dilute Solutions. By S. U. Pickering (*Ber.*, **24**, 1469).—A preliminary notice of results obtained on the freezing points of aqueous and benzene solutions of non-electrolytes containing 1·6 to 0·02 mols. of the dissolved substance to 100 mols. of the solvent. In one or two cases only, is the depression proportional within the limits of experimental error to the strength of the solution, and in most cases it increases with the dilution, becoming notably greater than the value given by Van't Hoff's equation, just as in the case of solutions of electrolytes, although the excess is smaller than with the latter. It is only with a particular strength of solution, and with a strength which is different with different substances, that Van't Hoff's equation expresses the true results. Marked irregularities also were noticed in some cases in the rate at which the depression increases with the strength. S. U. P.

Freezing Points of Dilute Aqueous Solutions of Non-electrolytes and Electrolytes. By J. Traube (*Ber.*, **24**, 1853—1859).—The author has determined the molecular reduction of the freezing point of water, caused by different typical electrolytes and non-electrolytes in solutions of varying concentration. The solutions contained from 2 to $\frac{1}{128}$ gram-mols. of dissolved substance per litre, and in every case the molecular reduction, which for non-electrolytes, at least, should remain constant, was found to increase with rising dilution. This increase is proportionately as great, or even greater, in the case of the non-electrolytes as in that of the electrolytes. From this the author concludes that the cryoscopic behaviour of solutions cannot be accepted as supporting the hypothesis of electrolytic dissociation in aqueous solution, since in this respect there is no essential difference between the behaviour of electrolytes and that of non-electrolytes. H. C.

Electrical Conductivity and Freezing Point. By J. Traube (*Ber.*, **24**, 1859—1864).—In a former paper (this vol., p. 255), the author endeavoured to show that the simple relation said by Arrhenius to exist between the electrical conductivity and the reduction of the freezing point had no experimental foundation. This he now further supports by showing that non-electrolytes, such as cane-sugar, urea, and phenol, have a definite molecular conductivity, which increases with the dilution, and, therefore, the value of $i = 1$, which Arrhenius assumes for these substances, must be incorrect. It is also shown that in the case of electrolytes the values obtained for i vary enormously with the concentration, and in no cases in which the values calculated from the conductivity and those from the freezing point of solutions of the same concentration were compared, was an agreement between the two sets of numbers observed. H. C.

The Cryoscopic Behaviour of Aqueous Cane-sugar Solutions. By J. F. EYKMAN (*Ber.*, **24**, 1783—1785).—The author has repeated the experiments of Traube (this vol., p. 824) with regard to the freezing point of cane-sugar solutions, and finds, contrary to Traube's results, that the depressions with different concentrations are perfectly normal. H. G. C.

The Theory of Dissociation into Ions, and its Consequences. By S. U. PICKERING (*Phil. Mag.* [5], **32**, 20—27).—The dissociationists, in opposition to Arrhenius' original view, now hold that the dissociation of compounds evolves heat, the evolution being due to the combination of electric charges with the atoms. The author raises the question as to the origin of such charges in the absence of the expenditure of external energy and the absence of friction, induction, and contact difference of potential: also how an affection of matter (a charge) can combine with matter to produce heat, and itself remain *in statu quo;* how the opposite electrification of the different atoms can, contrary to the older electro-chemical theory, dissolve the union between them. He characterises both this view, and that of the ions being allotropic atoms with less internal energy than ordinary atoms, as an hypothecation of a new form of matter to satisfy a theory which is inconsistent with known matter, or a verbal alteration designed to conjure away a stock of energy, so that the theory may not be said to be contradicted by the principle of the conservation of energy.

Dilution is held to increase dissociation, and, since in the case of calcium nitrate heat is thus absorbed, gaseous calcium nitrate should, on dissolving, absorb heat, for it thereby becomes dissociated; but this can not be true, for it can be shown that gaseous calcium nitrate would evolve heat on dissolution.

The author contrasts the present dissociation hypothesis with that of Clausius, which requires only the presence of a few atoms freed by accidental superheating, or else the continual interchange of atoms between contiguous molecules. The presence of any free atoms however, he considers as opposed to the fact that molecules of the elements are not formed in solutions, and suggests that polarisation currents may be explained by a coating of oriented molecules, not atoms. S. U. P.

Association versus Dissociation in Solutions. By S. U. PICKERING (*Ber.*, **24**, 1579).—When xH_2SO_4 is dissolved in yH_2O, the dissociation theory represents the acid as becoming partially dissociated into ions, so that the solution consists of more than $x + y$ units, whereas, on the association theory, the acid and water combine together to a certain extent, so that there are less than $x + y$ units present; by its effect on the freezing point of acetic acid the number of acting units can, according to the physical theory, be determined, and is found to be *less* than $x + y$, and less even than y alone; this was found to hold good for the weakest as well as the strongest solutions. Aqueous solutions of hydrochloric acid and of calcium chloride gave similar results; whilst with aqueous solutions of phosphoric acid and of nitric acid, as well as with alcoholic solutions of calcium chloride and nitrate, the acting units present, although less than $x + y$, were not less than y alone. According to the author's views, the actual composition of the compounds present cannot be ascertained by this method, and if the second solvent (the one which is frozen) has a much greater affinity for the dissolved substance than the first solvent has, the depression observed will be practically equal to that which would be produced by the substance and first solvent if they acted independently: this was found to be the case when the freezing point of sulphuric acid was depressed by aqueous acetic acid, and that of acetic acid by aqueous alcohol. S. U. P.

Reduction of the Results of Experiments with Special Reference to the Hydrate Theory of Solution. By S. LUPTON (*Phil. Mag.* [5], **31**, 418—429).—A criticism of part of Pickering's work on sulphuric acid solutions (Trans., 1890, 64 and 331).

Reduction of the Results of Experiments. By S. U. PICKERING (*Phil. Mag.* [5], **32**, 90—98), and by E. H. HAYES (*Phil. Mag.* [5], **32**, 99—104).—Replies to Lupton's criticisms. (See also Proc., 1891, 105—109.)

Objections to the Work on Sulphuric Acid Solutions. By S. U. PICKERING (*Chem. News*, **64**, 1, 2).—A further reply to objections raised in the discussion (Proc., 1891, 105—109) on the author's work on this subject.

Solutions of Double Salts. By J. E. TREVOR (*Zeit. physikal. Chem.*, **7**, 468—476).—This paper deals with the question of the relative solubilities of two salts which are capable of forming a double salt with one another, when mixed in varying proportions and brought into contact with water. The salts taken were potassium and copper sulphates, and the temperature at which the experiments were conducted was 25°. The solubility of copper sulphate alone in parts per 100 of water is 22·29, that of potassium sulphate 12·04, and that of the double salt 11·14. If excess of both salts is treated with water, or if a saturated solution of the two at a higher temperature is cooled down to 25°, it will be found in each case that the maximum solubility is obtained in 30 minutes, when the solution contains 15·6 grams of solid salt to 100 of water. After this, the solubility decreases, but in no case was it observed to fall to that of the double salt. At the point of maximum solubility, the solid salt is found to contain $5{\cdot}2K_2SO_4$ and $10{\cdot}4CuSO_4$. The proportions calculated on the assumption that each salt is present in the solution in the same proportion as in their saturated solutions would be $5{\cdot}41K_2SO_4$ and $10{\cdot}13CuSO_4$. Hence the solubility of the more soluble salt is greater and that of the less soluble salt is less in the solution of the two than in pure water, a result which, as Noyes has shown (this vol., p. 142), may be predicted from Nernst's theory of solubility. If the saturated solution of one of the salts is added to the saturated solution of the other, the double salt, being less soluble than either of the others, separates out, and this continues until equilibrium is established, when no further separation takes place. This result is in keeping with Nernst's experiments on salts which contain a common ion (Abstr., 1890, 3), but contradicts Rüdorff's assertion that potassium and copper sulphates displace one another in their concentrated solutions. Rüdorff (Abstr., 1888, 899) also found that if potassium and copper sulphates are allowed to diffuse from a solution in contact with the solid salts, the diffusate will be found to contain the two salts in the proportions in which they are present in the double salt. From this he concludes that the double salt diffuses without decomposition. This view the author shows is incorrect, for, on analysing the solution which is left behind in the dialyser, it is found to contain a greater proportion of copper sulphate than that originally present, and this result explains the above apparent diffusion of the double salt. For the potassium sulphate in the first instance diffuses more rapidly than the copper sulphate, and the latter is therefore left behind in the dialyser. The copper sulphate in the dialyser becomes more and more concentrated, until at length, owing to its concentration, it diffuses as rapidly as the potassium sulphate. The two will then be found in the diffusate in equivalent proportions, but each salt diffuses separately, and not as the double salt, and it remains very doubtful whether the double salt can exist at all in solution. H. C.

Influence of Inorganic Potassium Salts on the Solubility of Potassium Hydrogen Tartrate. By C. Blarez (*Compt. rend.*, **112**, 808—811).—The author has previously shown (this vol., p. 676) that the solubility of potassium hydrogen tartrate, in moderately strong solutions of potassium chloride at different temperatures, can be represented by the formula $Q_t = 0{\cdot}05 + 0{\cdot}000005t^3/\sqrt{K}$, where K is the quantity of potassium existing in the form of chloride. He now finds that this formula holds good for the bromide, iodide, chlorate, and nitrate. In other words, the effect depends solely on the weight of potassium present, and is independent of the nature of the acid with which it is combined; the effect of the various salts is proportional to their respective molecular weights. C. H. B.

Influence of Potassium Halides on the Solubility of Normal Potassium Sulphate. By C. Blarez (*Compt. rend.*, **112**, 939—942).—The solubility of potassium sulphate between 0° and 30° is represented by the equation

$$S_t = 8{\cdot}5 + 0{\cdot}12t.$$

If a saturated solution is mixed with successive small quantities of a potassium halide, a certain quantity of potassium sulphate is precipitated, but the sum of the salts in solution continually increases until a reverse action begins and the potassium sulphate affects the solubility of the halide. There is no simple relation between the quantity of potassium sulphate remaining in solution and the mass of the halide added; at a given temperature, however, the sum of the potassium sulphate in solution and the potassium in the salt added remains constant, so that K_2SO_4 diss. = const. − K in the halide.

The constant varies with the temperature, but between 0° and 30° the solubility of the potassium sulphate is represented by the equation

$$S_t = 7{\cdot}5 + 0{\cdot}1417t - K,$$

where K is the weight of potassium in the halide added. It is noteworthy that in this case, as with the hydrogen tartrate, the influence of the different potassium halides is proportional to their molecular weights. C. H. B.

Influence of Temperature on the Limits of the Explosion of Gaseous Mixtures. By J. Roszkowski (*Zeit. physikal. Chem.*, **7**, 485—499).—The author has investigated the conditions of the explosion of hydrogen, carbonic oxide, methane, and coal gas when mixed with oxygen or air, in different proportions, in the presence of an indifferent gas, such as carbonic anhydride, and at different temperatures. Dilution with an indifferent gas decreases the tendency to explode in gaseous mixtures; but this decrease is less the higher the temperature. This is probably due to the fact that the heat generated by combination of the two gases is largely used up in heating the indifferent gas present, instead of being employed in propagating the explosion. At low temperatures, methane will bear the greatest dilution without losing its power of exploding with oxygen, then come coal gas and hydrogen, and, lastly, carbonic oxide. At high temperatures (300°), the order is reversed. H. C.

The Dead-space in the Chloral-Soda Reaction. By E. Budde (*Zeit. physikal Chem.*, **7**, 586—600).—The figures drawn by Liebreich (*Zeit. physikal. Chem.*, **5**, 529—558; see also Abstr., 1890, 1207) to show the form of the dead-space in the chloral-soda reaction are compared by the author, who finds that the inferior surface makes in all cases an angle of about 150° with the glass walls. This signifies, in the author's opinion, that emulsions have a special coefficient of capillarity, and therefore a special mean surface-tension. The chloroform produced in the reaction he supposes to evaporate from the free surface of the liquid, and the lower boundary of the dead-space is that surface where the loss of chloroform by diffusion and evaporation exactly balances the production of chloroform by the interaction of the chloral and sodium carbonate. Various arguments are adduced to support the evaporation theory, the author considering unnecessary the assumption, made by Liebreich, that the mobility of the liquid molecules is diminished at measurable distances from the free surface. J. W.

The Factors of Energy. By W. Meyerhoffer (*Zeit. physikal. Chem.*, **7**, 544—585).—Any form of energy can be decomposed into two factors: for example, electrical energy = quantity × potential, energy of gases = volume × pressure.

The author gives the general equation:—Energy = content (*Inhalt*) × potential, and enunciates the following principle:—"The energy-contents of the ultimate particles of matter are equal." He proceeds to show that nearly all known stoichiometric regularities are particular cases of this rule, and that all known methods of determining molecular weights are based on one and the same principle, that, namely, of finding what masses possess the same energy-content.

The second law of thermodynamics is next discussed, and the author concludes that, in its ordinary form, it is untenable, there being no fundamental difference between heat and any other form of energy, the apparent distinction resting merely on the fact that we cannot attain zero-potential (the absolute zero of temperature) in the case of heat-energy, whilst this is possible for other forms. Some considerations on the general conditions of equilibrium follow, and the author concludes by identifying his "heat-content" with the "calorique" of Carnot, and by contesting the existence of energy as substance. J. W.

Inorganic Chemistry.

Volumetric Composition of Water. By E. W. Morley (*Amer. J. Sci.* [3], **41**, 220—231 and 276—288).—By the electrolysis of dilute sulphuric acid and most careful purification, hydrogen was obtained containing no impurity other than nitrogen in amount large enough to be detected. The amount of nitrogen present was never more than one-hundredth of a cubic centimetre in 2 litres of hydrogen, and was always determined in the gas used. An apparatus for the measurement of the gases was constructed, and is described in the paper, in which the mean error of measurement of the volume of hydrogen and oxygen used in the experiments was less than 1 part in 50000. With this 20 experiments were made, which gave a maximum value of 2·00047, a minimum value of 2·00005, and a mean value of 2·00023 volumes of hydrogen to unit volume of oxygen for the composition of water. H. C.

Preparation of Hydrobromic Acid. By M. Fileti and F. Crosa (*Gazzetta*, **21**, 64—65).—The authors have found the following process convenient and economical for the preparation of considerable quantities of hydrobromic acid:—A mixture of 1 part of red phosphorus, 2 parts of water, and sufficient sand to form a paste, is introduced into a flask, 10 parts of bromine then gradually added by means of a funnel provided with a stopcock, the flask gradually warmed, and the mixture of hydrogen bromide and bromine vapour passed through a deep glass jar filled with a mixture of red phosphorus and asbestos, impregnated with concentrated hydrobromic acid. Every trace of bromine vapour is thus effectually retained, and the process is continuous, and requires no supervision beyond an occasional shaking of the flask. S. B. A. A.

Two New Modifications of Sulphur. By Engel (*Compt. rend.*, **112**, 866—868).—One volume of sodium thiosulphate solution, saturated at the ordinary temperature, is poured, with continual agitation, into 2 vols. of a solution of hydrochloric acid, saturated at 25—30°, and cooled to about 10°. Sodium chloride is precipitated, and the thiosulphuric acid is so far stable that the liquid can be filtered. The filtrate is at first colourless, but soon becomes yellow, the intensity of the colour gradually increasing, as if a soluble sulphur establishes equilibrium in the decomposition of the thiosulphuric acid; sulphurous anhydride is evolved at the same time. When the liquid has acquired a deep-yellow colour, but while it is still quite transparent, it is agitated with its own volume of chloroform, which becomes yellow, whilst the colour of the aqueous solution becomes less intense. If the chloroform is allowed to evaporate, orange-yellow crystals of sulphur are obtained, quite different from octahedral sulphur; they have been examined by Friedel (next abstract). They are denser than octahedral sulphur (sp. gr. = 2·135), and at first are transparent, but in three or four hours they increase in volume, and pass gradually into the state of amorphous insoluble sulphur. They melt below 100°, and pass into the condition of the pasty sulphur from the thiosulphates and become partially soluble in carbon bisulphide.

If the solution of thiosulphuric acid in hydrochloric acid is allowed to remain, sulphur separates as a yellow, flocculent precipitate, completely soluble in water. The solution is yellow, and decomposes very rapidly, giving the ordinary pasty sulphur of the thiosulphates. The original precipitate gradually agglomerates, and passes into the same insoluble form without any evolution of hydrogen sulphide.

These phenomena are probably due to the gradual condensation of sulphur from an atomic to a polyatomic form. C. H. B.

Crystalline Form and Optical Properties of Engel's Crystalline Modification of Sulphur. By C. FRIEDEL (*Compt. rend.*, **112**, 834—835).—The crystals are rhombohedral, and belong to the hexagonal system; with converging polarised light, they show the cross and rings of birefractive uniaxial substances. The rhombohedron is very obtuse; *pp* (normal) = 40° 50′. It is noteworthy that tellurium crystallises in rhombohedral forms. C. H. B.

Volatility of Sulphuric Acid at Ordinary Temperatures. By A. COLEFAX (*Chem. News*, **63**, 179).—G. A. Koenigs has noticed that skeleton crystals of metallic iron, placed on a watch glass, supported on an iron triangle, in an ordinary desiccator containing sulphuric acid, had, after nine months, become coated with a white crust of anhydrous ferrous sulphate, and regards this as an indication of the volatility of sulphuric acid at the ordinary temperature of the air. This view finds support in the behaviour of the neutral compound obtained by the author of the present note from phenuvic acid (Trans., 1891, 190); this white, crystalline substance, when supported in a watch glass on a glass triangle over sulphuric acid in a perfectly clean ordinary desiccator, becomes rapidly brown and moist, a behaviour which it does not exhibit when exposed either over phosphoric anhydride or calcium chloride, or in an atmosphere containing sulphurous anhydride or nitrous fumes. D. A. L.

Formation of Dithionic Acid from Sodium Sulphite. By A. HOLST and R. OTTO (*Arch. Pharm.*, **229**, 171—177).—Malschevski and Sokoloff (*J. Russ. Chem. Soc.*, 1881, i, 169) showed that by the gradual addition of a dilute solution of iodine in potassium iodide to a dilute solution of hydrogen sodium sulphite, dithionic acid was produced to the extent of 20 per cent. of that theoretically possible. Doubt has been thrown on the above statement; but the authors' results confirm it. In their last experiment, 20·4 per cent. of the theoretically possible amount of dithionic acid was obtained. To estimate the amount of dithionic acid in its salts, it is only necessary to heat an aqueous solution with hydrochloric acid until all sulphurous anhydride is expelled, and then to precipitate the sulphuric acid in the residue with barium chloride. J. T.

Sulphuryl Peroxide (Holoxide). By M. TRAUBE (*Ber.*, **24**, 1764—1770; compare Abstr., 1889, 940).—It is not possible to isolate sulphuryl peroxide (holoxide) from its solution in 40 per cent. sulphuric acid by precipitating the sulphuric acid with barium carbonate, as the peroxide, not being capable of existence in pure water, then undergoes decomposition with the evolution of oxygen and the formation of hydrogen peroxide. When, however, the solution is diluted with 2—4 times its volume of water, and freshly-prepared barium phosphate added, the filtrate contains sulphuryl peroxide (holoxide) and barium phosphate dissolved in phosphoric acid; the amount of active oxygen is then determined by adding ferrous sulphate and titrating the excess with potassium permanganate, and that of sulphuric anhydride by boiling the solution with barium chloride and weighing the barium sulphate precipitated; the ratio of the weights of active oxygen and sulphuric anhydride is thus found to be 1 : 5, which agrees with the empirical formula SO_4. When the electrolysed 40 per cent. sulphuric acid, containing the sulphuryl peroxide (holoxide), is diluted with 1—2 vols. of water, and saturated with alkali at −10°, the peroxide remains practically undecomposed, so that alkali sulphates appear to exercise a protective influence on it; when, however, the solution is boiled for about half an hour, it ceases to give a blue colour with zinc iodide-starch, and becomes acid. It follows, therefore, that the compound is not the anhydride of an acid, or it would have formed the salt K_2SO_5 when saturated with potassium hydroxide, and this would then have decomposed into normal potassium sulphate and oxygen on boiling. Quantitative determinations of the amount of active oxygen in the neutralised solution, by adding potassium iodide and titrating with potassium thiosulphate, and also of the sulphuric acid produced on boiling it, by titrating with alkali, employing rosolic acid as indicator, gave, as a mean result, the ratio 1 : 4·85. When the active oxygen is determined by the ferrous sulphate method (see above), a higher value is obtained, which, when compared with the alkalimetric determination of the sulphuric acid, gives another ratio; this is explained as follows:—A large quantity of alkali, which always contains carbonates, being necessary to saturate the sulphuric acid solution of the peroxide, a certain amount of the hydrogen carbonate (which, owing to its neutral reaction, escapes detection) is invariably produced; when, however, the solution is boiled, a portion of the resulting sulphuric acid is neutralised by the hydrogen carbonate, and thus a low result is obtained by the alkalimetric method; the hydrogen carbonate exerts an influence in the opposite direction on the iodometric determination of the active oxygen, and the two errors compensating each other the correct ratio is preserved. It is, therefore, obvious that when the alkalimetric determination of sulphuric acid is compared with the accurate determination of the active oxygen by the ferrous sulphate method, a different ratio will be obtained. When the solution of the peroxide in 40 per cent. sulphuric acid (6—10 c.c.) is saturated by the very gradual addition of 33·3 per cent. sodium hydroxide solution at −15°, a slight excess of sulphuric acid and water, free from carbonic anhydride (100 c.c.), added to the crystalline mass, and after evaporation of the solution in the desiccator, and renewed dilution with water (100 c.c.), the active oxygen is determined by the ferrous sulphate method, and the acidity before and after boiling by titrating with standard alkali (the difference between the two giving the acid produced by the decomposition of the anhydride), the ratio 1 : 4·4 is obtained.

Sulphuryl peroxide (holoxide) is the analogue of the peroxides of organic acids discovered by Brodie. Berthelot's compound S_2O_7 is, perhaps, formed by the union of sulphuryl peroxide (holoxide) and sulphuric anhydride. According to Berthelot, his compound is decomposed by water with the evolution of oxygen, but it dissolves in not too dilute sulphuric acid without the evolution of oxygen. The author suggests that in the latter case it may react with the water present, forming sulphuric acid and sulphuryl peroxide (holoxide), $S_2O_7 + H_2O = H_2SO_4 + SO_4$, and this explains his observation that such a solution is identical with the solution of sulphuryl peroxide (holoxide) in not too dilute sulphuric acid prepared by electrolysis.

A. R. L.

Boron Hydride. By P. SABATIER (*Compt. rend.*, **112**, 865).—Magnesium boride is prepared by heating boric anhydride with magnesium powder in iron dishes in an atmosphere of hydrogen. The product is a brown mass, which is rapidly attacked by hydrochloric acid, leaving a slight residue of amorphous boron. The gas liberated by the action of the acid has an intensely disagreeable odour, burns with a beautiful green flame, and with silver nitrate solution, yields a brown precipitate soluble in nitric acid. When passed through a glass tube heated to dull redness, a ring of boron is deposited, and the issuing gas is ordinary hydrogen. In contact with potash there is a slight increase of volume, and the residual gas consists of pure hydrogen; water acts on the gas very slowly; mercury is attacked by it, and becomes covered with a brown layer. Electric sparks decompose it, leaving pure hydrogen.

This product (the boron hydride of Jones) is clearly hydrogen mixed with a very small proportion of boron hydride. C. H. B.

Boron Triiodide. By H. MOISSAN (*Compt. rend.*, **112**, 717—720).—Boron triiodide is obtained (1) by passing a mixture of hydrogen iodide and boron chloride vapour through a porcelain tube heated to redness; (2) by the action of iodine on boron at 700—800°, and (3) by the action of hydrogen iodide on amorphous boron. The last method gives the best results. Amorphous boron, dried in hydrogen at 200°, is heated in a current of dry hydrogen iodide in a Bohemian glass tube at a temperature approaching the softening point of the glass. Boron triiodide sublimes in large lamellæ, which have a purple-red colour, owing to the presence of a small quantity of iodine. When the crystals are dissolved in carbon bisulphide, and the solution is agitated with mercury, it becomes colourless, and on evaporation deposits colourless crystals, which, however, rapidly become coloured when exposed to light.

Boron triiodide is extremely hygroscopic, and is decomposed by the water which it attracts. It melts at 43°, and when it cools contracts and crystallises very readily; at 210°, it boils without decomposition, and if the vapour is heated to redness in a glass tube it burns when brought into contact with the air, iodine being liberated. It is very soluble in carbon bisulphide, benzene, and carbon tetrachloride, and is slightly soluble in phosphorus chloride, arsenic chloride, and many organic liquids.

Boron triiodide is decomposed immediately by water, yielding boric and hydriodic acids; it is not affected by hydrogen at a cherry-red heat, but burns when heated in oxygen, and is rapidly attacked by melted sulphur. Phosphorus interacts with it in the cold, with vivid incandescence, but silicon has no action at a dull-red heat. Sodium has no action at 50°, nor even at 210°, but at a red heat interaction takes place with incandescence.

Magnesium is attacked at 500°, with incandescence, but aluminium is not affected. Silver has no action at 500°, but silver fluoride interacts at the ordinary temperature, with incandescence and formation of silver iodide and boron fluoride. Phosphorus oxychloride, chloroform, and many organic liquids also produce an energetic reaction. Alcohol decomposes at once, and yields ethyl iodide and boric acid, $3EtOH + BI_3 = H_3BO_3 + 3EtI$. Ether yields ethyl iodide, boric acid, and alcohol. C. H. B.

Action of Hydriodic Acid on Boron Bromide. By A. BESSON (*Compt. rend.*, **112**, 1001—1003).—At the ordinary temperature no action takes place, but, by passing a current of hydrogen iodide containing boron bromide vapours through a glass tube heated to 300—400°, the substitution products BBr_2I, $BBrI_2$, and BI_3 are obtained. The yield is very small; the triiodide is easily separated from the other products, which can only be isolated with difficulty. The iodide and bromiodides are rapidly decomposed by air and light; light alone appears to be unable to effect the decomposition, the mechanism of which appears to be as follows:—The atmospheric moisture sets free hydriodic acid, which, in presence of light and the oxygen of the air, is decomposed with liberation of iodine. They are decomposed by water with violence. The bromiodide, BBr_2I, is a colourless liquid, distilling at about 125°. The second product, $BBrI_2$, is a similar substance, distilling at about 180°. W. T.

Boron Sulphide. By P. SABATIER (*Compt. rend.*, **112**, 862—864).—Boron sulphide was prepared by the action of hydrogen sulphide on amorphous boron at a red heat. The product is carried forward by the excess of gas, and condenses in different forms in different parts of the apparatus. Near the hottest part of the tube it is fused, and becomes opalescent when cold; further away it forms an opaque porcelain-like mass, with a slight nacreous lustre and a conchoidal fracture; in the coolest part of the tube it forms brilliant, very light needles. These needles are pure boron sulphide, B_2S_3; the vitreous product always contains an excess of sulphur, varying from 11 to 17 per cent. All the forms of boron sulphide are attacked by water with very great violence, with formation of boric acid and hydrogen sulphide, the heat developed ($B_2S_3 = 118$ grams) being 58 Cal. with the acicular sulphide, and 56 Cal. with the vitreous sulphide. Solution of the sulphide in iodine solution develops +124·6 Cal., and from this the decomposition by water would develop +58·6 Cal. The mean value is +57·8 Cal.

From these results, it follows that B_2 amorphous + S_3 solid = B_2S_3 solid, develops +82·6 Cal., a number lower than the heat of formation of a corresponding quantity of oxide or chloride; lower even than the heat of formation of the iodide. As a matter of fact, iodine has no action on boron sulphide in the cold, but decomposes it at a dull-red heat, with formation of brown lamellæ, which seem to be identical with the iodide described by Moissan. C. H. B.

Boron Selenide. By P. SABATIER (*Compt. rend.*, **112**, 1000).—Boron selenide is prepared by passing a slow regular current of dry hydrogen selenide over boron, maintained at a bright-red heat, in a hard glass tube. The brownish-black boron is entirely transformed into the yellowish-grey boron selenide without fusion, a little of the compound only being deposited in a pulverulent state on the tube beyond the boat. The selenide is much less fusible and volatile than the corresponding sulphide. Water acts violently on the grey boron selenide, disengaging hydrogen selenide, and at the same time liberating some red, pulverulent selenium; hence, doubtless, the disgusting odour of the substance is due to the action of atmospheric moisture.

The yellow, pulverulent selenide deposited beyond the boat is decomposed by water without deposition of selenium; hence its composition is doubtless comparable with that of the sulphide, and would be represented by B_2Se_3; this conclusion is borne out by the results of a rapid analysis of the compound. The author will determine the heat of combination of this selenide as well as that of boron telluride.

W. T.

Action of Hydrogen Bromide on Silicon Chloride. By A. BESSON (*Compt. rend.*, **112**, 788—791).—Hydrogen bromide, mixed with vapour of silicon chloride, was passed repeatedly through a red-hot tube, and the product was digested with mercury and fractionated. Silicon bromotrichloride, $SiBrCl_3$, was easily purified by fractionation; it boils at +80°, and does not solidify at −60°. With ammonia, it yields a white, amorphous compound, $2SiClBr_3,11NH_3$, and with hydrogen phosphide at 0° under 25 atmos., or at $-22°$ under 17 atmos., it also forms a solid compound.

The chlorotribromide and the dichlorodibromide could not be separated by fractionation; but the former solidifies at $-39°$, whilst the latter does not solidify even at $-60°$.

Silicon chlorotribromide, $SiClBr_3$, melts at $-39°$, and boils at 126—128°. It shows a great tendency to remain in superfusion, even at $-50°$. With ammonia, it yields a white, amorphous compound, $2SiClBr_3,11NH_3$, readily decomposed by water.

Silicon dichlorodibromide yields with ammonia a white, amorphous compound, $SiCl_2Br_2,5NH_3$, which is decomposed by water.

The products of the interaction of the haloïd acids and boron halides are under investigation. C. H. B.

Potassium Persulphate. By H. Marshall (*Proc. Roy. Soc. Edin.*, **18**, 63—64).—A mixture of cobaltous sulphate, potassium sulphate, and sulphuric acid, when submitted to electrolysis in a divided cell, yields crystals of potassium persulphate. Also the same compound is obtained when potassium hydrogen sulphate is electrolysed under the same conditions. The salt dissolves readily in hot water, but, if boiled, oxygen is evolved; it appears to be isomorphous with potassium permanganate; experiments on the electrical conductivity of the solution show that the formula is KSO_4; it forms no precipitate with barium salts; with silver nitrate, silver peroxide is produced; hydrochloric acid gives chlorine, and strong nitric or sulphuric acid yields oxygen highly charged with ozone.

E. W. P.

Sodium. By M. Rosenfeld (*Ber.*, **24**, 1658—1660).—Sodium, which when kept under mineral oil has become covered with a crust, is easily purified by immersing in a mixture of amyl alcohol (1 part) and petroleum (3 parts) and rubbing with a rag soaked in the same mixture until it acquires a silvery lustre. It is then laid in petroleum containing 5 per cent. of amyl alcohol, washed with pure petroleum, and kept in petroleum containing 0·5 to 1 per cent. of amyl alcohol. The bright metal becomes slowly covered with a film of sodium amyloxide, which is, however, easily rubbed off with filter paper. Potassium and lithium can be purified in the same way and then keep their metallic lustre for a long time.

Sodium cleaned as above combines at once with mercury with evolution of light. The liquid alloy of sodium and potassium is easily prepared by pressing together the two clean metals under a mixture of amyl alcohol (1 part) and petroleum (9 parts). Sodium sulphide is also easily prepared by rubbing the clean metal (1 gram) and salt (3 grams) to a fine powder, and then mixing with sulphur (0·7 gram), care being taken to avoid any pressure. When the two substances are intimately mixed, combination suddenly takes place with evolution of light. If the mixture of sodium powder and salt be mixed with sulphur in the proportions required to form di- or trisulphide, the reaction takes place more quickly and violently.

Selenium and tellurium behave in the same way as sulphur when mixed with sodium powder. E. C. R.

Argentous Compounds. By GÜNTZ (*Compt. rend.*, **112**, 861—862).—When dry hydrogen chloride is passed over silver subfluoride (Abstr., 1890, 1055), the latter becomes violet, and when the action has reached its limit, the product has the composition Ag 83·35 to 84·08; Cl 15·07 to 14·19 (calc. for Ag_2Cl, $Ag = 85·88$; $Cl = 15·12$). Carbon tetrachloride, silicon tetrachloride, phosphorus chloride, &c., behave in a similar manner and yield silver subchloride, Ag_2Cl, and the corresponding fluoride. The author has prepared the subiodide by the action of hydrogen iodide; the subfluoride by the action of hydrogen sulphide; and the suboxide by the action of water vapour at 160°. C. H. B.

The Cause of the Slight Solubility of Chemically Pure Zinc in Acids. By J. M. WEEREN (*Ber.*, **24**, 1785—1798).—The slight solubility of pure zinc in dilute acids is usually explained by supposing that the solution of impure zinc is in reality due to the electric currents set up by the contact of the zinc with the impurities, and that as in pure zinc no such currents can occur, it remains undissolved. This theory does not, however, account for the solubility of the pure metal in nitric acid, or even in dilute sulphuric or hydrochloric acid at their boiling points, and the author has, therefore, again investigated the subject. As the result of his experiments he finds that the insolubility of the pure zinc is due simply to the formation of a condensed layer of hydrogen on the surface, which then prevents the further action of the acid. In the case of nitric acid, this layer is oxidised by the acid as it forms, and cannot protect the surface of the metal, whilst in the case of impure zinc, the hydrogen is evolved from the surface of the more electro-negative impurities according to the usual law, thus leaving the surface of the zinc exposed to the action of the acid.

The experiments were made with chemically pure zinc and sulphuric acid, the latter being diluted with 20 parts of pure water. It was proved that even such simple means as brushing the surface of the zinc caused a considerable increase in the quantity dissolved. This became much more striking when the reaction was allowed to take place in a vacuum, the relation of the mean quantity dissolved under atmospheric pressure and in a vacuum being 1 : 6·6. The quantity of impure zinc dissolved under similar conditions was found to undergo very little change.

In the next series of experiments, the quantity of pure zinc dissolved by the acid at different temperatures was determined. The quantity dissolved in 30 minutes increased regularly from 2·1 milligrams at 0° to 9·3 milligrams at 98°, but as soon as 100° was reached and ebullition commenced the quantity rose to 122·1 milligrams. This is in full agreement with the author's theory, as the evolution of bubbles, which start for the most part from the zinc plate, would naturally affect the hydrogen film and expose fresh surfaces of the zinc to the action of the acid. If the temperature be raised above 100° by increasing the pressure, the quantity of zinc dissolved is not appreciably more than at 98° so long as ebullition does not take place. The quantity of impure zinc dissolved is not appreciably affected by the ebullition of the liquid.

The addition of chromic acid and of hydrogen peroxide to the acid also causes a great increase in the solibility of the pure zinc, the former causing an increase in the ratio 175 : 1, and the latter in the ratio 306 : 1, a result which is again strongly in favour of the author's theory. These oxidising agents do indeed also increase the solubility of impure zinc, but to a much smaller extent, the ratio for chromic acid being 6·5 : 1, for hydrogen peroxide 3·5 : 1.

Similar results have been obtained with cadmium, cobalt, iron, and aluminium. The latter, which is as a rule almost insoluble in dilute acids, dissolves readily in a vacuum, and also dissolves under similar conditions in neutral ferric chloride solution, the latter being reduced to ferrous chloride by the hydrogen evolved. H. G. C.

Determination of the Molecular Weights of some Metals. By G. MEYER (*Zeit. physikal. Chem.*, **7**, 477—484).—The author has determined the molecular weights of a number of metals by measuring the E.M.F. of cells containing two amalgams of the metal in question of different concentration as electrodes and a salt of the metal as electrolyte (comp. Türin, Abstr., 1890, 1046). If E is the E.M.F. measured, the molecular weight may then be obtained by means of the equation $M = 1·1908\, qT/E \times \log_{10} c_1/c_2$, where c_1 and c_2 are the concentrations of the two amalgams, q is the electrochemical equivalent of the metal, and T is the absolute temperature. In this way the molecular weights of zinc, cadmium, lead, tin, copper, and sodium were determined at ordinary temperatures. All these metals were found to have monatomic molecules. H. C.

Magnesium Lead Iodide. By R. OTTO and D. DREWES (*Arch. Pharm.*, **229**, 179—181).—Magnesium carbonate was dissolved in aqueous hydriodic acid and the solution evaporated until a skin formed on the surface; then as much dry lead iodide was added as the liquid would take up. On filtering hot and allowing to remain until cold, a copious deposit of crystals of magnesium lead iodide, $PbMg_2I_6 + 16H_2O$, was obtained. The honey-yellow salt loses its water of crystallisation at 140° and becomes citron-yellow. Above 150°, it decomposes with separation of iodine. Like the corresponding chloride, it is exceedingly hygroscopic. In the air it quickly becomes a magnesium iodide lye, containing lead iodide in suspension. Water decomposes it into soluble magnesium iodide and insoluble lead iodide. Exposed to hydrogen sulphide, it immediately gives rise to lead sulphiodide, which afterwards passes into lead sulphide. The crystals belong to the rhombohedral system. J. T.

Earths of the Cerium and Yttrium Groups. By A. BETTENDORFF (*Annalen*, **263**, 164—174).—The brown oxide (RO = 113·2—114) obtained from orthite as already described (Abstr., 1890, 851) contains didymium, samarium, gadolinium, and terbium; when it is submitted to a further systematic partial decomposition of the nitrates, the didymium accumulates in the last fractions, as its nitrate is relatively the most stable, and, after a number of operations, didymium oxide (RO = 110·76) can be isolated from the mixture. The first fractions yield a yellow, or reddish-yellow oxide (RO = 118—119·5) the concentrated solution of which does not give the absorption lines of didymium at all, but shows those of samarium in a very marked manner; when a concentrated neutral solution of the nitrate of this oxide (RO = 118—119·5) is mixed with a warm saturated solution of potassium sulphate, no separation takes place for some hours, and then a yellowish, crystalline powder, consisting principally of potassium samarium sulphate, is deposited. From this salt, an almost colourless earth, having the equivalent 116·49, can be isolated, whilst there remains in solution the double salt of a yellowish-red earth (RO = 119·96) containing terbium and gadolinium but only very small quantities of samarium.

By fractionally precipitating with very dilute ammonia the nitrate of the crude samarium oxide, prepared from the potassium samarium sulphate, the oxide can be obtained in a colourless condition. The atomic weight of samarium was determined by submitting the nitrate of this colourless oxide to fractional decomposition and converting the first, fifth, and ninth fractions into the sulphate; the first fraction gave RO = 115·97, but the fifth and ninth gave concordant results, namely, RO = 116·05 and RO = 116·06 respectively, from which the atomic weight of samarium is calculated to be 100·06 (O = 15·96, S = 31·98), or $R''' = 150·09$.

The pure samarium earth is colourless, and has in a high degree the property of emitting light when it is heated to a high temperature on platinum wire, giving a luminous spectrum in which are observed bright lines, corresponding exactly with the dark bands in the absorption spectrum of its solution; the wave-length measurements of five of these bright lines and a diagram of the spectrum are given.

On comparing the spectrum of glowing samarium earth with the absorption spectrum of a solution of a samarium salt, it is seen that in the former there are present bright lines with which there are no corresponding dark lines in the absorption spectrum; the same phenomenon was observed by Bahr and Bunsen in the case of erbium earth.

The absorption spectrum, obtained by passing the light emitted from zirconium oxide heated in the oxyhydrogen flame through a plate (1·5 mm. in diameter) of a crystal of samarium sulphate, is unusually sharp, the six bands of the absorption spectrum of a solution of the salt being separated into twelve well-defined lines; the measurements of the wave-lengths of these lines and a diagram of the spectrum are given, as are also those of the spark spectrum of samarium chloride.

All the observations made in the course of the author's investigation of samarium earth tend to show that it is a definite chemical compound; if, as is held by some chemists, it is really a mixture of several earths having almost identical properties, it is improbable that the methods at present employed for the separation of the rare earths will be successful in the case of samarium earth.

Samarium earth has not the property of phosphorescence (luminescence), but pure lanthanum earth, which has been strongly ignited, shows a bright-green phosphorescence, the spectrum of which exceeds, in beauty and intensity, the flame spectrum of calcium chloride; a diagram of, and measurements of the wave-lengths of the various lines in the phosphorescent lanthanum earth spectrum are given.

F. S. K.

Amalgams. By J. SCHUMANN (*Ann. Phys. Chem.* [2], **43**, 101—125). —The author has prepared a large number of amalgams of different metals. The original object was to determine the thermal changes attending the formation of these amalgams, but, owing to the fact that their dissolution in acids only takes place very slowly, this had to be abandoned. On the other hand, it was noticed that after a time a change took place in many of the amalgams, in some cases leading to the formation of crystals, whilst with others, even those containing difficultly oxidisable metals, a separation into metallic oxide and mercury took place. Several of the amalgams were examined dilatometrically, in order to ascertain the changes in volume which take place with change of temperature, and particularly with the change from the solid to the liquid condition. It was noticed that on cooling, and also on again heating, the amalgams occupied a greater volume than when first heated. A definite melting or solidifying point was not observed, but the melting was in all cases a gradual one and the solidification still more gradual. An amalgam on being heated, cooled, and then again heated, will be found to melt at a lower temperature than at first, but if a considerable time is allowed to elapse between the first and second heating, the second melting point will then be found higher than the first. A great increase in volume takes place on melting. From the results, the author concludes that solid amalgams consist of different crystalline modifications, some of which are stable at a given temperature and others unstable, and that, under certain circumstances, the latter will be transformed into the former. An interesting instance of this is furnished by sodium amalgam. On being melted and allowed to cool in a vertical tube, the amalgam, on solidification, separated into four different layers, one of which consisted of long, thick, prismatic needles, and the others of fine needles or were without definite crystalline form. The composition of the first layer was found to be Na_2Hg_{10}, and in course of time, this layer was found to increase in volume, so that in half a year the whole contents of the tube were found to have changed into this compound, with the separation of a small quantity of a liquid amalgam.

H. C.

Ammoniacal Mercuric Chlorides. By G. ANDRÉ (*Compt. rend.*, **112**, 859—861).—When 1 part of yellow mercuric oxide is boiled with 5 parts of ammonium chloride dissolved in 17·5 parts of water, a small quantity of a crystalline precipitate forms on cooling; its composition varies, but approaches to $HgCl_2,2NH_3$. If the mother liquor is mixed with excess of ammonia, a white, curdy precipitate separates, and this, when washed rapidly by decantation and dried at 100°, has the composition $N_2H_6HgCl_2 + NH_2HgCl$. The same compound is obtained in sealed tubes at 100° with only a small quantity of ammonia. If the curdy precipitate is subjected to prolonged washing, it is converted into a compound of the chloramide and the chloride, $NH_2{\cdot}Hg{\cdot}O{\cdot}HgCl$, the latter being the ultimate product of the action of water.

If the curdy precipitate is heated with excess of ammonia in sealed tubes at 200°, it yields a crystalline product which, when washed with a very small quantity of water, has the composition $N_2H_6HgCl_2$. The mother liquor, when mixed with a large quantity of water, yields a white precipitate of the compound $NH_2{\cdot}Hg{\cdot}O{\cdot}HgCl$.

If a cold solution of ammonium chloride containing free ammonia is mixed with mercuric chloride, the precipitate at first redissolves, but on continued addition of mercuric chloride to the *cold* liquid, a white, curdy precipitate separates, and this, when dried at 100°, has the composition $HgCl_2,NH_3$. The same product is obtained with a hot solution, provided that mercuric chloride is added in excess; it is decomposed by water with formation of the chloramide.

C. H. B.

Basic Magnesium and Zinc Chromites and Normal Cadmium Chromite. By G. VIARD (*Compt. rend.*, **112**, 1003—1006).—These compounds have been prepared in the dry way (I) by calcination of the chromate, (II) by the action of potassium dichromate on the oxide, or (III) by the action of potassium dichromate or chromate on the chloride. The residue is in each case treated with boiling hydrochloric acid and washed by decantation.

Magnesium Chromites.—(*a*) A clear brown powder of the formula $2MgO,Cr_2O_3$ formed at a red heat by method I; (*b*) a grey-yellow substance of the composition $5MgO,4Cr_2O_3$, formed at the melting point of silver by method I; (*c*) at a very high temperature the same substance is obtained as (*b*), but its colour is greyish-green; (*d*) a brown powder, $3MgO,2Cr_2O_3$, formed at a dull-red heat by method II.

The third method is believed by the author to be incapable of yielding pure products, as the oxygen liberated readily attacks magnesium chloride, setting free chlorine, which, as shown by Fremy, acts on alkaline chromates at a red heat yielding chromic oxide. The vapour of magnesium chloride passed over strongly heated potassium chromate gives a crystalline product which, under the microscope, is seen to consist of lamellæ of chromium oxide and octahedra of magnesium chromite.

Zinc Chromites.—I. Zinc chromate slowly decomposes at 440° yielding a violet-black powder, $3ZnO,2Cr_2O_3$ (*a*). As the temperature is raised, zinc oxide separates out, and, at a very high temperature, the product obtained approaches the normal chromite in composition; the colour changes just as in the case of the magnesium compounds.

By method II, a reddish-brown powder is obtained represented by $6ZnO,5Cr_2O_3$ (*b*), whatever the proportions of oxide and dichromate taken. By method III, mixtures of the two products (*a*) and (*b*) are usually obtained. The author has previously shown (Abstr., 1889, 1111) that the normal chromite is obtained in regular octahedra by passing the vapour of zinc chloride over potassium chromate maintained at a white heat.

Cadmium Chromite.—The normal chromite is obtained as a green powder at any temperature above a red heat. The crystalline substance may be obtained by passing the vapour of cadmium chloride over strongly heated chromate. W. T.

New Oxygen Compound of Molybdenum. By E. Péchard (*Compt. rend.*, **112**, 720—722).—It is well known that hydrogen peroxide produces an orange coloration when added to a solution of an alkaline molybdate, but the nature of the product has not been investigated.

Molybdic acid, which is insoluble in water and in acids, dissolves readily when gently heated with hydrogen peroxide, forming a yellow liquid, and the product of the action of hydrogen peroxide on molybdic acid or alkaline molybdates gives no precipitate with phosphoric acid. Ammonium paratungstate behaves like molybdic acid, and readily dissolves in hydrogen peroxide, whilst solutions of alkaline tungstates that have been mixed with hydrogen peroxide no longer give precipitates with acids.

Potassium trimolybdate dissolves in hydrogen peroxide, forming an orange-yellow solution which, when concentrated at a gentle heat, deposits beautiful, yellow crystals (seemingly triclinic) of the composition $K_2O,Mo_2O_7,4H_2O$. When heated gently in a vacuum, they lose water and oxygen, and leave a white residue of acid potassium molybdate. The yellow compound is soluble in hot water, but is only slightly soluble in alcohol.

Ammonium molybdate, when evaporated with hydrogen peroxide at 100°, yields yellow crystals (seemingly monoclinic) of the analogous compound $(NH_4)_2O,Mo_2O_7,4H_2O$, very soluble in water, but insoluble in alcohol. When carefully heated in a vacuum, ammonia, water, and nitrogen are evolved and molybdic acid is left.

Molybdic acid, when evaporated in a vacuum with hydrogen peroxide, yields only a reddish-yellow, amorphous residue insoluble in water.

The potassium and ammonium salts are decomposed by alkalis with evolution of oxygen; hydrochloric acid, when heated with them, evolves chlorine; potassium iodide rapidly turns brown, owing to the liberation of iodine. The two salts are derived from a new higher acid of molybdenum, permolybdic acid, Mo_2O_7,xH_2O. C. H. B.

New Oxygen Compound of Tungsten. By E. Péchard (*Compt. rend.*, **112**, 1060—1062).—A solution of sodium paratungstate, when boiled for a few minutes with hydrogen peroxide, assumes a yellowish tint and no longer gives any precipitate with nitric acid. When evaporated in a vacuum, a syrupy liquid remains which deposits small, white, radiating crystals of the formula $Na_2O,W_2O_7,2H_2O$. The crystals are more soluble in water than sodium paratungstate, and give off water when heated in a vacuum, finally decomposing with evolution of oxygen if the heating be continued.

Ammonium paratungstate yields a similar salt. Alkalis destroy these salts with liberation of oxygen. Solutions of the new salts liberate iodine from potassium iodide and chlorine from hydrochloric acid.

These oxygenated compounds are hypertungstates analogous to the hypermolybdates (preceding abstract). W. T.

Thiovanadates. By G. KRÜSS and K. OHNMAIS (*Annalen*, **263**, 39—72).—In this paper the authors give a rather more complete account of the methods of preparation and properties of various thiovanadates, all of which have been previously described (compare Abstr., 1890, 1381). F. S. K.

Mineralogical Chemistry.

Formation of Graphite by Contact Metamorphosis. By R. BECK and W. LUZI (*Ber.*, **24**, 1884—1886).—Graphite occurs in many different associations in nature. Quite recently the authors have discovered some beautifully crystallised graphite in rocks which have been metamorphosed by contact with ancient volcanic rocks; the graphite crystals are easily discernible from the amorphous carbonaceous substances of the original clay slates and siliceous slates. Mention is made in the literature of the apparent occurrence of graphite in certain slates metamorphosed by granite, but analytical and crystallographic data are wanting. The authors have now proved that graphite has been formed from carbonaceous substances by contact metamorphosis in the case of certain rocks in Saxony. In Pirna and Kreischa, upper Silurian clay slates and siliceous slates occur, which are very rich in carbonaceous substances, and lie partially within the region of contact of the granite and hornblende-granite; those within this region of contact have become converted into graphitic rocks. A chiastolite slate and a graphitic quartzite were examined. The former occurred imbedded in the much metamorphosed grey trap of Burkhardt Forest; whilst the latter turned out to be a true contact rock from the immediate vicinity of the granite in Röhrsdorfer Valley, Kreischa; both have been formed from original siliceous slates, and their composition and structure show that they are true contact products. The graphite from the chiastolite slate formed completely opaque, jagged lumps having a metallic lustre by reflected light, and measuring between 0·003 and 0·02 mm.; whilst the carbonaceous particles in the unaltered upper Silurian clay-slates and siliceous slates were almost too small to measure (below 0·001 mm.). There were also some isolated perfect hexagonal crystals. The quartzite was still richer in graphite, which, moreover, occurred in more beautiful crystals; viewed under a lens, the quartzite appeared to consist of a crystalline mixture of quartz and graphite. The graphite frequently existed as hexagonal crystals, some having plain faces and some rounded. Single well formed crystals measured 0·03 mm. It occurred most frequently, however, in jagged, ramified, irregular, crystalline aggregates of 0·3 mm. from which sometimes crystallographically perfect individual crystals grew out. The graphite had a greasy feeling, and produced a metallic streak; it had also a metallic lustre. Analysis showed that the graphite from the chiastolite slates had the composition $C = 98{\cdot}84$ per cent., $H = 0{\cdot}21$ per cent.; whilst that from the graphitic quartzite had the composition $C = 99{\cdot}94$ per cent., $H = 0{\cdot}05$ per cent. The graphitic quartzite itself contained over 2 per cent. of graphite, and its specific gravity was 2·62—2·637.

Proof is therefore afforded by this discovery that graphite is formed in nature from amorphous carbon in much the same manner as it is produced artificially. A. R. L.

Action of Dry Hydrogen Sulphide on Metals; Synthesis of Minerals. By R. Lorenz (*Ber.*, **24**, 1501—1510).—The author has previously observed that when zinc sulphide containing ammonium chloride is strongly heated, the zinc sulphide volatilises and is obtained from the sublimate in a crystalline condition. Corresponding experiments made with ferrous sulphide containing ammonium chloride gave similar results (see also Weinschenk, *Zeit. für Kryst.*, **17**, 486). This volatilisation is due to the fact that when the mixture is heated, ammonia, zinc chloride, and hydrogen sulphide are formed, and the two last-named compounds then react together on cooling with formation of crystallised zinc sulphide. This is proved by the fact that the vapours given off when ammonium chloride is heated and driven over zinc sulphide, if quickly cooled, deposit considerable quantities of zinc chloride. The method is, therefore, in principle identical with that of Durocher (*Compt. rend.*, **32**, 823), the presence of ammonia gas being of no importance.

Led by these experiments, the author has also examined the action of dry hydrogen sulphide on different metals; the reaction with silver has, however, been previously studied by Deville and Troost (*Compt. rend.*, **52**, 920), who succeeded in thus obtaining silver-glance. When the dry gas is passed over a bundle of iron wire heated to a temperature rather below the melting point of the sulphide, the wire became covered with a layer of crystallised iron sulphide, which, on crystallographic investigation, proved to be troïlite; the quantity of sulphur in the different parts is, however, not quite constant. If dilute hydrogen sulphide be employed, the crystals are more sharply developed, and appear to be hexagonal and hemimorphic.

Nickel, under similar circumstances, does not yield crystals of millerite, but forms a crystalline crust of nickel sulphide. The vapour of zinc on the other hand, readily reacts with dry hydrogen sulphide forming a conglomerate of wurtzite crystals, which are also hemimorphic. Cadmium vapour acts still more readily, so that the reaction may be carried out in an ordinary combustion tube. The product is a mixture of hexagonal greenockite crystals with a hitherto unknown modification of cadmium sulphide which forms monosymmetric twin crystals. H. G. C.

Artificial Formation of Daubreelite. By S. Meunier (*Compt. rend.*, **112**, 818—820).—Hydrogen sulphide is passed at a red heat, over (1) a mixture of ferrous chloride and chromic chloride; (2)

finely powdered native chrome iron ore; or (3) an alloy of iron and chromium. The alloy of iron and chromium (Abstr., 1890, 568) gives the best results. Pyrrhotine is formed in distinct hexagonal crystals, and when this is removed by treatment with hydrochloric acid, a black, crystalline powder is left, which has the composition and all the properties of natural daubreelite, $FeCr_2S_4$. The powder consists of irregular angular grains with distinct and brilliant cleavage faces, but very little indication of any specific forms; sp. gr. = 5. It dissolves in nitric acid and had the composition, in one case, S 45·01; Fe 19·99; Cr 35·0 = 100·00.

The simultaneous formation of pyrrhotine is of great interest since the two minerals are constantly found associated in meteoric iron. The results afford further evidence in support of the view that holosiderites are formed by the interaction of gases. C. H. B.

Artificial Production of Hyalite at the Ordinary Temperature. By S. Meunier (*Compt. rend.*, **112**, 953—954).—A porous cell containing Nordhausen sulphuric acid is placed in a syrupy solution of sodium silicate; in less than 48 hours all the alkaline silicate is replaced by a granular, hyaline, colourless, and fragile substance. Prolonged boiling with successive quantities of ordinary sulphuric acid removes all the sodium, and washing with boiling water removes the sulphuric acid without otherwise affecting the product.

The product contains 5·69 per cent. of water, but it is evident that all the grains are not hydrated to the same extent; when strongly heated, some become opaline and opaque, whilst others remain hyaline and transparent. The latter, although soluble in concentrated alkaline solutions, act strongly on polarised light; they have no crystalline form, but the planes of fracture recall cleavage planes and give elongated forms, the optical extinction following the direction of the elongation Many of the fractures are conchoidal, and the general properties of these hyaline granules agree with those of the opal of Pont-du-Château.

Amongst the portions that are not affected by a bright-red heat are thin plates with parallel surfaces often more than 10 mm. broad, resembling lamellæ of glass. Between crossed Nicols they show a crowd of black crosses similar to those shown by spherulitic opal.

C. H. B.

Artificial Periclase; A Product of the Magnesium Chloride Industry. By R. Otto and J. H. Kloos (*Ber.*, **24**, 1480—1482).—Artificial periclase is formed under certain conditions in the furnaces in which magnesium oxychloride is heated for the preparation of hydrochloric acid and chlorine. In the course of repairing one of the muffle furnaces used for this purpose, large blocks of magnesia were removed, which, on examination, were found to contain druses filled with crystals of periclase. These varied in size from almost microscopic crystals to octahedra having an edge 4 mm. in length, and showed a strong diamond lustre. In the larger crystals, the edges were frequently rounded off by a combination with a forty-eight sided figure, these having usually a yellowish-grey colour, but the smaller crystals were for the most part sharply developed and colourless.

Two specimens were analysed with the following result :—

	I.	II.
MgO	98·21	97·94
Fe_2O_3	1·57	1·70

The specific gravity was found to be 3·555 and 3·571, which is considerably less than that of the natural periclase (3·75), and also of Rose's artificial preparation (3·644), this being probably due to the fact that they contain less iron. The crystals show a very distinct cubical cleavage and have a hardness between that of felspar and quartz. H. G. C.

Chromite. By H. Pemberton, Jun. (*Chem. News*, **63**, 241—242).—On the Pacific Coast of the United States there are several deposits of chromite, and it is found throughout the Santa Lucia mountains and the coast hills of San Luis, Obisbo Co., California, in serpentine rocks in greater or less masses, existing as loose and fragmentary rocks in the ravines and as pockets and veins on the mountains; a sample obtained from the Pick and Shovel mine, located on the South Fork of Chorro Creek, at an elevation of 1800 feet, gave the following numbers on analysis :—

Cr_2O_3.	Al_2O_3.	Fe_2O_3.	MgO.	FeO.	MnO.	SiO_2.	H_2O.	Total.
52·68	11·40	3·52	16·23	11·77	0·15	3·40	0·94	100 09

Deducting the water and the magnesia and silica due to gangue, the numbers for the pure mineral became—

Cr_2O_3.	Al_2O_3.	Fe_2O_3.	MgO.	FeO.	MnO.
56·96	12·32	3·81	14·02	12 73	0·16

from which is deduced the relationship

$$R_2O_3 : RO = 1·00 : 1·02.$$

To decompose the mineral, it is mixed with sodium carbonate, heated over night by a Bunsen burner in a loosely-covered crucible, and the next morning it is heated for an hour over a blast lamp, stirring frequently. The ferrous oxide was determined by dissolving in sulphuric acid, sp. gr. 1·34, in a closed tube, under pressure.

D. A. L.

Crystallised Azurite from Arizona. By O. C. Farrington (*Amer. J. Sci.*, **41**, 300—307).—The author has made a detailed crystallographic study of the crystals of azurite from Arizona. Altogether 21 forms were observed on these crystals, four of which are new. The axial ratio deduced from the measurements made is $a : b : c = 0·85676 : 1 : 0·88603$; $\beta = 87° 36'$. This result differs but little from that deduced by Schrauf from his measurements of crystals from European localities. B. H. B.

Ferro-goslarite, a New Variety of Zinc Sulphate. By H. A. Wheeler (*Amer. J. Sci.*, **41**, 212).—In a zinc mine at Webb City, Jasper Co., Missouri, there occurs a new variety of goslarite, containing about 5 per cent. of ferrous sulphate. It appears as incrustations on the wall of a large body of zinc blende. Analysis shows that the mineral is a double sulphate of zinc and iron, in the ratio of 4·9 per cent. $FeSO_4$, to 55·2 $ZnSO_4$, or nearly 1 to 11. As the properties of the mineral correspond closely to those of goslarite, the author has given it the name of ferro-goslarite. B. H. B.

Halotrichite from Colorado. By E. H. S. BAILEY (*Amer. J. Sci.*, **41**, 296—297).—This mineral was found in the Elk mountain range, Pitkin Co., Colorado, and, as no record could be found of the description of this mineral from an American locality, the author has submitted it to analysis. The results were as follows:—

SiO_2.	SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	Total.
0·42	33·46	12·98	1·60	5·19	0·17	46·04	99·86

It is, therefore, essentially a sulphate of aluminium and iron, with part of the alumina replaced by ferric oxide, and part of the ferrous oxide replaced by magnesia. B. H. B.

Occurrence of Pollucite at Hebron, Maine. By H. L. WELLS (*Amer. J. Sci.*, **41**, 213—220).—The author announces the discovery of pollucite, the mineral originally termed pollux by Breithaupt, in a new locality. Hitherto this rare mineral has been found only on the island of Elba. Its composition adds greatly to its interest, as it is the only known mineral of which cæsium is an essential constituent. Analysis of pollucite from the new locality at Hebron, Maine, gave the following results:—

H_2O.	SiO_2.	Al_2O_3.	CaO.	Cs_2O.	K_2O.	Na_2O.	Li_2O.	Total.
1·53	43·48	16·41	0·21	36·77	0·47	1·72	0·03	100·62

From this the formula $H_2R_4Al_4(SiO_3)_9$ is calculated. A comparison of all the ratios calculated from the published analyses of pollucite, makes it probable that the new formula can be assigned also to the Elba mineral. B. H. B.

Pink Grossularite from Mexico. By C. F. DE LANDERO (*Amer. J. Sci.*, **41**, 321—323).—The occurrence of pink garnets at Xalostoc, in Mexico, has been known for some years, but the locality had not been properly explored, the specimens obtained being merely from the surface. Analysis of very pure crystals, obtained in January of this year, gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.
40·64	21·48	1·57	35·38	0·75

The formula is $(CaMg)_3(Al_2Fe_2)Si_3O_{12}$. The crystals are rhombic dodecahedra, with a sp. gr. of 3·516, and a hardness of 7·5.

B. H. B.

Occurrence of Xenotime as an Accessory Constituent of Rocks. By O. A. DERBY (*Amer. J. Sci.*, **41**, 308—311).—In the examination of the heavy residues obtained by concentration in the gold-washer's pan of crushed samples of a large number of Brazilian crystalline rocks, the rare mineral xenotime has been found to be a fairly constant accessory of the muscovite granites. The xenotime occurs in the well-known octahedral form, with the prismatic faces barely noticeable. Samples of muscovite granite from 21 different localities were tested, and of these 14 gave xenotime, always accompanied by zircon, and in all but three cases by monazite. The almost constant occurrence of these cerium and yttrium phosphates in the Brazilian rocks suggests the hypothesis that they will be found in similar rocks all over the world. B. H. B.

Magnetite Ore Districts in Brazil. By O. A. DERBY (*Amer. J. Sci.*, **41**, 311—321).—The districts of Jacupiranga and Ipanema afford instances of what appears to be a hitherto unnoticed mode of occurrence and association of magnetic iron ores. In specimens of nearly pure ore from the former district, the magnetite forms a continuous network enclosing detached grains of pyroxene in part altered to mica. This peculiar rock is distinguished as *jacupirangite.* The rocks included under this title present the various types of pure magnetite, magnetite with accessory pyroxene, pyroxene with accessory magnetite, and pyroxene and nepheline with biotite and olivine as accessory or essential constituents. The gradual passage from one type to another has been satisfactorily proved. At Ipanema, a rock of similar composition cuts the carboniferous strata. B. H. B.

Occurrence of Sulphur in Marine Muds and Nodules, and its bearing on their Mode of Formation. By J. Y. BUCHANAN (*Proc. Roy. Soc. Edin.*, **18**, 17—39).—The examination of muds obtained from the bottoms of various seas showed that they are, as a rule, nearly black, owing to the presence of ferrous sulphide: this blackness is, however, not found on the immediate surface layer, because the sulphide in presence of water and oxygen is oxidised, sulphur being set free, and the dark blue changed to a reddish colour. The presence of ferrous sulphide is ascribed to annelids who, in search of food, pass the mud through their bodies, and thus the sulphates present are converted into sulphides; at the same time the coarser particles are rendered finer. All the deep-sea muds and manganese concretions, when fresh, yield ammonia when heated, demonstrating the presence of organic matter; when such "blue mud" is dried, no sulphide is to be found, but the mass is permeated with fine particles of ferric oxide. The free sulphur was estimated by digestion with chloroform, and weighing the residue after evaporation. By far the largest percentage of sulphur was found in clay from the Sound of Jura, the quantity amounting to 0·4 per cent.; a radiolarian ooze from the North Pacific, at a depth of 2900 fathoms, contained 0·0031 per cent.; the percentages of sulphur in other muds is given in a table.

The method employed to estimate the ferrous sulphide was based on the reaction of ferric chloride in excess on the sulphide, whereby ferrous chloride is formed, the amount produced being estimated by potassium permanganate; other ferrous compounds present were estimated by treatment of the mud with hydrochloric acid and titrating with permanganate. E. W. P.

Action of Metallic (and other) Salts on Calcium Carbonate. By R. Irvine and W. S. Anderson (*Proc. Roy. Soc. Edin.*, **18**, 52—54).—Corals were exposed to the action of solutions of manganese, zinc, chromium, mercury, and tin chlorides, iron sulphate, nickel, cobalt, copper, lead, and silver nitrates, and ammonium phosphate. The action of salts of nickel and cobalt was very slow, whilst that of copper and manganese was rapid. In most cases there is a direct interchange, the oxide of the metal taking the place of the lime. With ammonium phosphate, the interchange was between the carbonic anhydride of the coral and the phosphoric anhydride of the phosphate; it is probable that this reaction accounts for the formation of calcium phosphate deposits through the excreta of birds deposited on coral or calcium carbonate, but only in rainy climates, for without water the change does not occur. Silver and mercury salts are deposited as oxides. E. W. P.

Manganese Deposits in Marine Muds. By R. Irvine and J. Gilson (*Proc. Roy. Soc. Edin.*, **18**, 54—59).—The authors do not consider the present theories of Buchanan and Murray as sufficiently or correctly accounting for manganese nodules found in sea mud. They base their new theory on the following experiment:—When ferrous and manganous carbonates were mixed with decomposing mussel flesh, the mass became black and evolved hydrogen sulphide: air was then blown through the mixture for 12 hours, after which no manganese was found in the solid residue, whilst all the iron had been converted into sulphide; they therefore conclude that the formation of manganese sulphide cannot be a result of the animal life, or the decomposition of animal matter, at the sea-bottom, for carbonic anhydride must always be present in excess. Buchanan does not give proofs of presence of manganese sulphide, but relies on the analogy of manganese to iron. E. W. P.

Composition of some Deep-Sea Deposits from the Mediterranean. By J. Y. Buchanan (*Proc. Roy. Soc. Edin.*, **18**, 131—138).—The muds of which analyses are given were collected on the line of the telegraph cable between Marseilles and Algiers; the depths at which they were collected vary from 265 to 1536 fathoms. The methods of analyses are stated; the SiO_2 was found to vary from 14·79 to 44·37 per cent.; Fe_2O_3, 3·45 to 6·64; Al_2O_3, 1·30 to 12·30; $CaCO_3$, 18·3 to 47·1; loss on ignition, 2·90 to 10·89; further analytical details are given. E. W. P.

Silica and the Siliceous Remains of Organisms in Modern Seas. By J. Murray and R. Irvine (*Proc. Roy. Soc. Edin.*, **18**, 229—258).—Analyses of sea-water show that only 1 part of silica is contained in 200,000 to 500,000 parts of sea-water, so that it is inconceivable that diatoms and other forms of life obtain the silica necessary for their growth from the water. It appeared probable, however, that the silica was derived from the suspended clay, and this idea received considerable support from the fact that waters of high salinity contain less suspended mud than those of low salinity; moreover, higher temperatures prevent suspension of matter, it being also known that siliceous organisms are more abundant in shore waters, or in waters of low salinity and in cold waters, as for instance diatoms in brackish waters, and in those of the cold southern and Polar seas, and radiolaria in Polar waters, and in the West Pacific and East Indian oceans, where there is a relatively low salinity. There are other theories propounded to explain the source of soluble silica, but the authors are still experimenting, with the view of definitely settling the question. E. W. P.

Organic Chemistry.

Formation of Ethers in the Preparation of Isoallylene and its Homologues from the corresponding Halogen Derivatives and Alcoholic Potash. By W. VAUBEL (*Ber.*, **24**, 1685—1695).—Isoallylene, $CH_2{:}C{:}CH_2$, can be prepared by three methods, namely, by the electrolysis of potassium itaconate, by the action of sodium on β-chlorallyl chloride, and by the action of zinc-dust and alcohol on dibromopropylene, $CH_2{:}CBr{\cdot}CH_2Br$. By the action of alcoholic potash on allyl bromide, allyl ethyl ether is formed, together with a small quantity of isoallylene. The present paper deals with the behaviour of allyl halogen compounds with alcoholic potash.

Allyl Bromide.—If allyl bromide is added to concentrated alcoholic potash, at first only a small quantity of potassium bromide is precipitated; after five minutes, however, a violent reaction sets in, bubbles of isoallylene are given off, and heat is liberated in quantity sufficient to cause the boiling of the mixture. The semi-solid mixture which remains consists of potassium bromide, alcoholic potash, and allyl ethyl ether. Several experiments are described, with the object of determining the conditions under which the greatest yield of isoallylene is obtained. The results show that the best yield is obtained by using equivalent quantities of allyl bromide and alcoholic potash at 13°; 10 grams of allyl bromide then yield 66·5 c.c. of isoallylene. Raising the temperature, or the use of excess of potash or alcohol, reduces the yield considerably.

Allyl Chloride.—Equivalent proportions were used as with the bromide. The reaction takes place very slowly at the ordinary temperature (16°); on heating on the water-bath, 56 c.c. of isoallylene were obtained, whilst 6·1 grams of allyl chloride remained unaltered.

Allyl Iodide.—The reaction takes place slowly at the ordinary temperature. 10 grams of allyl iodide at 18° in one hour yielded 19 c.c. of isoallylene; at 100°, however, 115 c.c. was obtained.

The above reaction is not a convenient method for the preparation of isoallylene, since only 1 per cent. of the allyl bromide and 9 per cent. of the iodide is converted into it. The reaction probably takes place according to the equations $C_3H_5Br + KOH = C_3H_4 + KBr + H_2O$ and $C_3H_4 + EtOH = C_3H_5{\cdot}OEt$. It is not probable that the ether is formed first, and that this breaks up into alcohol and isoallylene. Experiments to settle this point gave the following results:—Allyl ethyl ether usually decomposes so as to yield allyl alcohol and ethyl alcohol, but even when boiled with alcoholic potash no reaction takes place.

If alcohol cooled below 0° be saturated with isoallylene, and the solution heated in sealed tubes with solid potash, first at 100°, and then at 150—170°, allyl ethyl ether is formed. The ether is not formed when isoallylene and ethyl alcohol are heated alone, but in this case a liquid is obtained which the author considers is a polymeride of isoallylene. It quickly resinifies on exposure to air, or by the action of dilute sulphuric acid, and gives a white precipitate with mercuric chloride. Allyl ethyl ether also gives a white compound when shaken with mercuric chloride.

Tetramethylisoallylene, $CMe_2{:}C{:}CMe_2$, is obtained by the action of alcoholic potash on the chloride $CHMe_2{\cdot}CCl_2{\cdot}CHMe_2$. It forms a white precipitate with mercuric chloride; and it is probable that this reaction is characteristic of isoallylene and its homologues. Isoallylene and its homologues cannot be obtained in any quantity from the corresponding alkyl halogen compounds and alcoholic potash; instead of the hydrocarbons, ethers are formed. There are, however, two exceptions, the hexine, $CMe_2{:}CH{\cdot}CH{:}CH_2$, which is obtained from dimethylallylcarbinyl chloride, and tetramethylisoallylene obtained as above.

The author sums up the results already obtained as follows:—(1.) When alkyl halogen compounds are decomposed with alcoholic potash, a hydrocarbon is always formed, but under certain conditions it is converted into an ether. (2.) Alkyl halogen compounds which already contain a double bond always yield a hydrocarbon containing a treble bond, even if the formation of a hydrocarbon with two double bonds is possible, thus, $CH_2{:}CBr{\cdot}CH_3 + KOH = CH{:}C{\cdot}CH_3 + KBr + H_2O$. (3.) Those halogen compounds which already contain a double bond, and ought to yield hydrocarbons with two double bonds, yield these hydrocarbons, but the greater part combines with the alcoholic potash to form an ether. If, however, the ether would be a tertiary ether, then the hydrocarbon remains unchanged, as is the case in the formation of tetramethylisoallylene. (4.) The ethers are not formed from an alcohol and the unsaturated hydrocarbon alone. It is necessary that alcoholic potash should be present. (5.) Isoallylene and its homologues, and the ethers obtained from them, yield white precipitates with mercuric chloride. This is proved for isoallylene, tetramethylisoallylene, and ethyl allyl ether. E. C. R.

Purification of Crude Alcohol. By E. MOHLER (*Compt. rend.*, **112**, 815—818).—The author has applied his methods of analysis (this vol., p. 503) to follow the rectification of crude alcohol from treacle. 80 per cent. of the total alcohol can be obtained free from higher alcohols or other poisonous compounds, the chief impurities being minute quantities of ethereal salts. The head products consist chiefly of aldehydes and ethereal salts, and are much purer than the tailings, which contain a large proportion of the higher alcohols, chiefly amyl alcohol, with a small quantity of aldehydes and ethereal salts of high boiling point. C. H. B.

The Fourth Primary Amyl Alcohol. By L. TISSIER (*Compt. rend.*, **112**, 1065—1068).—*Trimethylethyl alcohol* (*trimethylcarbincarbinol*), $CMe_3·CH_2·OH$, has not been previously prepared. The author some time ago obtained trimethylethylamine from tertiary butyl cyanide, and characterised it by its platinochloride (*Bull. Soc. Chim.* [3], **3**, 497). Freund and Senze, without acknowledging the priority of the author's work, obtained an alcohol boiling at 102—103° by acting on trimethylethylamine, prepared in the same way, with silver nitrite, and called it trimethylethyl alcohol. The substance obtained by them has properties identical with those of the tertiary amyl alcohol, dimethylethylcarbinol, $CMe_2Et·OH$, first obtained by Wurtz. Trimethylethyl alcohol is prepared by the reduction of trimethylacetic chloride with sodium amalgam. A mixture of 10 grams of the chloride with 20 grams of trimethylacetic acid is dropped on 250 grams of 3 per cent. sodium amalgam, and well agitated. After 24 hours, on addition of water, saturation with potash, and distillation, about 8 grams of an oily liquid is obtained, which can be fractionated into portions boiling at from 65—80°, 105—120°, 150—180°, and above 180°. The fraction passing over at 105—120°, when rectified, forms a crystalline mass without action on polarised light (compare trimethylacetic acid), which melts at 48—50°, boils at 112—113°, and exerts a considerable vapour tension, even at the ordinary temperatures. It dissolves in a very small quantity of ether, and has all the characters of an alcohol. It yields trimethylacetic acid on oxidation with chromic acid. The velocity and limit of etherification, determined at 153—154°, using equivalent proportions of glacial acetic acid and the alcohol, were as follows :—

Velocity .. 40·75; 40·69; 40·71. Limit .. 66·99; 67·2.

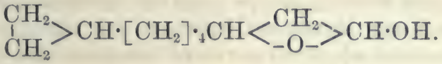
The fraction passing over between 150° and 180° on rectification yields *trimethylethyl trimethylacetate*, a colourless liquid of agreeable odour, boiling at 164—166°. On boiling with dry potash, it is rapidly decomposed into trimethylethyl alcohol and potassium trimethylacetate. By the action of glacial acetic acid, or of acetic chloride on trimethylethyl alcohol in sealed tubes, the *acetate* is obtained; it is a colourless liquid, boiling at about 126°, and having an odour of apples.

The first fraction obtained reduces ammoniacal nitrate of silver, and forms a compound with sodium hydrogen sulphite, from which, after purification, the *aldehyde* $CMe_3·COH$ may be prepared; it is a liquid boiling at 74—75°, melting at +3°, and having sp. gr. 0·7927 at 18°.

It is proposed to continue the study of trimethylethyl alcohol and its derivatives. W. T.

Constitution of the Oxygen Compounds in Petroleum. By R. ZALOZIECKI (*Ber.*, **24**, 1808—1815).—In this paper the author gives an account of the oxygen compounds obtained from petroleum in a works at Kolomea, and which were sent to him in the form of sodium salts. These were separated from the petroleum still present by repeated treatment with alkalis, and reprecipitation by acids; the resulting brown oil was treated with hydrogen chloride in alcoholic solution, and the mixture of ethyl salts thus obtained subjected to fractional distillation. Three of the fractions appear to be approximately homogeneous, and yield the corresponding acids on hydrolysis. From the analysis of both acids and ethyl salts, it would appear that the former have the composition $C_{10}H_{18}O_2$, $C_{11}H_{20}O_2$, and $C_{12}H_{22}O_2$, that is, they belong to a series having the general formula $C_nH_{2n+2}O_2$, which is in agreement with the results of previous investigators (this Journal, 1875, 248; *J. Russ. Chem. Soc.*, 1883, 237; Abstr., 1887, 648).

The compound $C_{10}H_{18}O_2$, on treatment with phosphorus and iodine, yields a substance containing iodine. The formula of the latter, as deduced simply from a determination of the iodine, is $C_{10}H_{17}IO$, and not $C_{10}H_{17}IO_2$, and hence the author concludes that these compounds do not contain the carboxyl group, but are hydroxylactones or lacto-alcohols, and proposes for the compound $C_{10}H_{18}O_2$ the following constitutional formula:—



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}>CH\cdot[CH_2]_4\cdot CH<\begin{matrix}CH_2\\-O-\end{matrix}>CH\cdot OH.$$

H. G. C.

Preparation of Disodium Erythroxide. By DE FORCRAND (*Compt. rend.*, **112**, 1006—1009).—The monosodium and monopotassium compounds have been previously described (see Abstr., 1890, 935). To prepare *disodium erythroxide*, $C_4H_8Na_2O_4,4H_2O$, three equivalents of soda are added to one equivalent of erythrol, both being in concentrated aqueous solution, and the mixture is allowed to evaporate for two or three days in presence of phosphoric anhydride; or powdered erythrol is dissolved directly in the most concentrated soda solution by a gentle heat. Stellate groups of crystals separate, which are freed from the mother liquor by draining on porous tiles. When heated at 135—140° in a current of hydrogen, the water is entirely driven off, and pure dry disodium erythroxide, $C_4H_8Na_2O_4$, remains as a white, amorphous, very hygroscopic mass. This is the first disodium alkyloxide that has been prepared pure.

If the quantity of soda be increased to five equivalents, crystals are obtained of the formula $C_4H_8Na_2O_4 + 2NaOH + 9{\cdot}5H_2O$. By a study of the thermal properties of this substance, it is evident that it is not a mixture. The anhydrous compound $C_4H_8Na_2O_4,2NaOH$, obtained as above described, decomposes at temperatures higher than 160°.

The first and second alcoholic hydrogen atoms are readily replaced by sodium, but the remaining two such atoms in erythrol are not removable in the same manner; this fact is of importance in connection with the constitution of polybasic alcohols, particularly as the author has previously prepared disodium glyceroxide, but has been unable to substitute the third alcoholic hydrogen by sodium.

The question suggests itself whether the secondary alcohols form true alcoholates, as it is already known that secondary aldehydes do not react with bases in the same way as do the primary aldehydes.

The author proposes to investigate isopropyl alcohol to ascertain this point. W. T.

Refractive Power of Levulose and Invert-sugar. By H. OST (*Ber.*, **24**, 1636—1645).—The differences in the refractive power of levulose observed by various chemists have led the author to carry out fresh determinations. The sugar employed was prepared from inulin, and was crystallised from absolute alcohol three or four times; the product is anhydrous, is not hygroscopic, and decomposes slowly at 100°. Heating is without effect on the refractive power of neutral aqueous or alcoholic levulose solutions.

For solutions containing 3 to 30 per cent. by weight of levulose the refractive power is given by the formula $(\alpha)20/D = -(91{\cdot}90 + 0{\cdot}111p)$, where p is the percentage of sugar in grams. These results are higher than those of Hönig and Jesser for solutions containing less than 25 per cent. of the sugar; for concentrations above this, the results are somewhat lower. The values of Jungfleisch and Grimbert are about 3 per cent. lower throughout, apparently pointing to the presence of some inactive impurity in their preparations.

A comparison was instituted between the actual refractive powers of various solutions of equal parts of levulose and dextrose, and the theoretical values calculated from the author's numbers for levulose and those of Tollens for dextrose; the agreement is very close, and the numbers would be almost identical if Tollens' figures should prove to be slightly too high, in consequence of some decomposition of the dextrose having taken place while being dried at 60—70°.

Comparative experiments were instituted to show the amount of monosaccharoses decomposed during the inversion of sucrose by means of hydrochloric acid, acetic acid, and oxalic acid of various concentrations and at different temperatures. Acetic acid decomposes levulose at ordinary temperatures, as does also 0·1 per cent. hydrochloric acid at 100°; the best results are obtained by heating the sugar at 60° for 1·5 hours with 2 per cent. solution of oxalic acid, or for 4 hours with 1 per cent. solution; the presence of the oxalic acid is without effect on the refractive power of invert-sugar.

The results of Grubbe are thus confirmed, whilst those of Jungfleisch and Grimbert are shown to be incorrect. J. B. T.

Trehalose. By MAQUENNE (*Compt. rend.*, **112**, 947—950).—Solutions containing 16 and 8 per cent. of trehalose solidify at −0·895° and −0·43° respectively, and hence the molecular weight is about 350, a result which shows that trehalose does not belong to the trioses.

Trehalose, completely inverted by sulphuric acid, was treated with phenylhydrazine and compared with a solution of glucose of equal reducing power in the manner previously described; they gave the same amount of glucosazone under the same conditions, and it follows that glucose is the sole product of the inversion of trehalose, and that the molecule of the latter contains C_{12}.

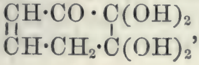
When boiled with excess of acetic anhydride in presence of a small quantity of zinc chloride, trehalose yields an octacetin,

$$C_{12}H_{14}O_{11}(C_2H_3O)_8,$$

which, after crystallisation from alcohol, melts at 97—98°, is distinctly volatile, burns with a beautiful white flame, and is rapidly hydrolysed by baryta at 100°.

It follows from these results that trehalose is an octohydric alcohol, isomeric with the true saccharoses, and very similar to maltose in its molecular constitution, but differing from the latter in that it has no aldehydic function. C. H. B.

Xylose from Maize Cobs. By W. E. Stone and D. Lotz (*Ber.*, **24**, 1657—1658).—If maize cobs are treated with 1 per cent. ammonia, and then extracted for eight hours with boiling sodium hydroxide (2 per cent.) and alcohol added to the extract, a brown, voluminous precipitate is obtained. $2\frac{1}{2}$ kilos. of material yield 200 grams of this product. The product dissolves in acids, and is precipitated on addition of alcohol; after being treated in this manner several times, it still contains 0·76 per cent. of ash. It is easily soluble, and blackens on exposure to air. When distilled with hydrochloric acid (sp. gr. $= 1·06$), it yields 48—50 per cent. of furfuraldehyde. When heated for eight hours with sulphuric acid (2 per cent.) on the water-bath, a sweet syrup is obtained which deposits crystals after a time. These were identified as xylose by determining their optical activity, $[\alpha]_D = 19·55°$, and by preparing the phenylhydrazide, which melts at 159—160°, and is strongly lævorotatory. The yield is small, and further experiments showed that most of the product yielding furfuraldehyde remains in the material. E. C. R.

Action of Nitric Acid on Vegetable Fibres. By C. F. Cross and E. J. Bevan (*Ber.*, **24**, 1772—1776; see also *Proc. Chem. Soc.*, 1891, 61).—In a recent paper (this vol., p. 814), Lifschütz has described the action of a dilute mixture of nitric and sulphuric acids on pine-wood, chiefly with a view to the preparation of pure cellulose, and without considering intermediate products obtained from the lignin constituents of the wood. From their researches in a somewhat wider field, although these are yet far from being completed, the authors are in a position to state that Lifschütz's conclusions cannot be applied to vegetable fibres in general. They have already shown in previous researches that with the typical lignocellulose jute fibre moderately concentrated acid yields yellow acid compounds with a small proportion of nitrogen (Abstr., 1880, 666), whilst with 5 per cent. nitric acid the fibres are converted into cellulose, oxalic acid, and gaseous products (Trans., 1889, 199). They have shown that the jute fibre contains a closed chain of carbon atoms, probably having the formula  $\begin{array}{l} CH\cdot CO\cdot C(OH)_2 \\ \| \qquad\quad\;\; | \\ CH\cdot CH_2\cdot C(OH)_2 \end{array}$, and that three of these have combined together by oxygen condensation, forming a complex of 18 carbon atoms.

When the fibres are heated with dilute nitric acid (5—10 per cent.) at 50—60°, a gas is evolved which consists for the most part of nitrous oxide, and only contains small quantities of nitric oxide; later on, the evolution of hydrocyanic acid is also observed, and on boiling the product with alkali, ammonia and more hydrocyanic acid are formed. Oxalic acid is also obtained, even at as low a temperature as 40—50°.

The reaction is extremely complicated, but it appears very probable that the substance is hydrolysed at the points where aldehyde condensation has taken place, nitrous acid being also formed, which then attacks the ketone ring with formation of oximes; these are then decomposed by excess of nitrous acid in the following manner:—

$$X\!:\!C\!:\!N\cdot OH + O\!:\!N\cdot OH = X\!:\!CO + N_2O + H_2O.$$

The result, therefore, is an increase in the number of oxygen atoms in the molecule, and the ring is then split with formation of compounds of lower molecular weight. The process is not to be regarded, with Lifschütz, as a simple oxidation.

In continuing these investigations, the authors also intend to examine the physiological side of the question. H. G. C.

Dissymmetry and Optical Activity of Alkyl Derivatives of Ammonium Chloride. By J. A. Le Bel (*Compt. rend.*, **112**, 724—726). —No physical isomerides have hitherto been obtained by the substitution of any number of alkyl radicles less than four for the hydrogen in ammonium chloride. This absence of isomerides may be due to one of two causes: firstly, only one of the isomerides geometrically possible may satisfy the necessary dynamical conditions of equilibrium and possess an invariable form; secondly, the radicles united to the nitrogen may be able to make permutations amongst themselves.

The action of moulds on methylethylpropylamine hydrochloride yields no product with any optical activity, and it follows that in this case the radicles are able to make permutations among themselves similar to those which take place at high temperatures in the case, for example, of sodium amyloxide.

The author has previously shown that an invariable geometric form of a molecule arises from repulsions between its constituent particles (*Bull. Soc. Chim.* [3], **2**, 788), and it would follow that by the introduction of more complex radicles with larger spheres of repulsion, stability might be given to a particular geometric form which, with simpler radicles, is unstable. This condition seems to be realised in trimethylisobutylammonium chloride (Abstr., 1890, 475).

Isobutylpropylethylmethylammonium chloride, when subjected to the action of moulds, gave two products, which in concentrated solution had rotatory powers exceeding −7° and −8°. The active salt is somewhat stable, and if neutral can be obtained in the solid form. It can be converted into an active acetate by means of silver acetate, but not into an active sulphate. The optical activity disappears when the mercurochloride or platinochloride is treated with hydrogen sulphide, but does not quite disappear in the case of the aurochloride. The alteration in the rotatory power in these cases is probably due to the action of the liberated hydrochloric acid. There is some indication of the existence of an isomeride with a dextro-rotatory power.

The action of moulds on the chlorides of ethylpropyldimethylammonium, ethyldipropylmethylammonium, ethyldipropylisobutylammonium, and ethylpropyldiisobutylammonium yields products which are either inactive or show very feeble optical activity. If any active isomerides exist, they form only a very small fraction of the products obtained under these conditions. C. H. B.

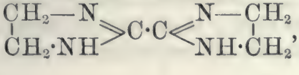
Action of Hydroxyhydrocarbon Derivatives on Nitrides and Hydronitrides. By R. VIDAL (*Compt. rend.*, **112**, 950—951).—When vapours of methyl or ethyl alcohol are passed over phospham, PN_2H, previously heated at 150—200°, a metaphosphate of a primary amine is formed, together with some alcohol and a secondary amine. The primary action is $PN_2H + 4ROH = PO_4(NH_2R_2)_2$, but the phosphate decomposes under the influence of heat in accordance with the equation $PO_4(NH_2R_2)_2 = ROH + PO_3NH_3R + NHR_2$.

The reaction is more distinct in sealed tubes; ether yields the same products as alcohol, but aldehyde yields resinous and ammoniacal products, the nature of which has not yet been determined.

Boron nitride seems to behave in a similar manner, and the behaviour of the higher alcohols, phenols, and polyhydric alcohols is under investigation. C. H. B.

Chloralimido-compounds. By R. MOSCHELES (*Ber.*, **24**, 1803—1805).—When chloralurethane, $CCl_3·CH(OH)·NH·COOEt$, is treated with benzoic chloride and aqueous alkali, it does not, as expected, yield the benzoyl compound $CCl_3·CH(OBz)·NH·COOEt$, but simply loses water forming *ethyl chloralimidocarboxylate*, $CCl_3·CH:N·COOEt$, which melts at 143°. Other acid chlorides and anhydrides have the same effect. Different substituted chloralimido-compounds can be prepared in a similar manner from the substituted chloral-ammonias having the general formula $CCl_3·CH(OH)·NHX$. The following derivatives have been prepared: *formylchloralimide*, $CCl_3·CH:N·CHO$, melting at 193°; *acetylchloralimide*, $CCl_3·CH:NAc$, melting at 207°; and *benzoylchloralimide*, $CCl_3·CH:NBz$, which decomposes at 142°. They are all insoluble in water, but dissolve readily in alcohol and acetic acid, and are distinguished by the ease with which they crystallise. On animals they have no physiological action whatever.

H. G. C.

Action of Ethylenediamine on Thiamides. By G. FORSSELL (*Ber.*, **24**, 1846—1847).—Dithioxamide combines with 2 molecules of ethylenediamine, ammonia being evolved and an intermediate compound of the formula $NH_2·C_2H_4·NH·CS·CS·NH·C_2H_4·NH_2$ probably first formed; this is, however, unstable, and immediately passes into the closed compound  $\begin{array}{l}CH_2—N\\ \mid\\ CH_2·NH\end{array}\!\!>C·C<\!\!\begin{array}{l}N—CH_2\\ \quad\ \mid\\ NH·CH_2\end{array}$, hydrogen sulphide being eliminated. This compound is a powerful base, and combines with two equivalents of acids to form stable salts.

In a similar manner, ethylenebenzyldiamine is prepared from ethylenediamine and thiobenzamide. Ethylenediamide also reacts with thiocarbamide, and with xanthogenamide, but the products have not yet been further investigated. J. B. T.

Action of Ethylenediamine on Ethyl Dibromosuccinate. By G. FORSSELL (*Ber.*, **24**, 1847—1848).—Ethyl dibromosuccinate is mixed with anhydrous ethylenediamine (2 mols.) in absolute alcoholic solution; after warming for some time on the water-bath, the crystals of ethylenediamine hydrobromide which separate are removed, and the alcohol allowed to evaporate spontaneously; the residue crystallises from alcohol in colourless needles, melts at 161°, and has the formula $COOEt\cdot C\vdots C\cdot CO\cdot NH\cdot C_2H_4\cdot NH_2$. The *potassium salt* crystallises in needles; the copper salt is very unstable.

Phenylpropiolic acid is formed by the interaction of ethyl cinnamate and ethylenediamine. J. B. T.

Derivatives of Amylene Nitrosate. By O. WALLACH and J. WAHL (*Annalen*, **262**, 324—339).—*Amylenenitrolamine*,

$$NH_2\cdot CMe_2\cdot CMe\colon NOH,$$

can be obtained by dissolving amylene nitrosate (Abstr., 1888, 37) in warm alcoholic ammonia, then adding a sufficient quantity of potassium carbonate to combine with the nitric acid present as ammonium nitrate, evaporating to dryness, and extracting the organic base with chloroform. It is, however, best prepared by dissolving amylene nitrosochloride (Abstr., 1888, 1098) in warm, concentrated alcoholic ammonia, filtering from the precipitated ammonium chloride and evaporating the alcohol under reduced pressure; the residue is then extracted with boiling chloroform, when the base passes into solution, whilst the hydrochloride of the base remains in an almost pure condition.

Amylenenitrolamine melts at 99—100°, boils at 218—220°, and sublimes when gently heated in long, lustrous needles; it is very readily soluble in water, alcohol, and chloroform, but more sparingly in ether, and insoluble in light petroleum. An aqueous solution of the base has a strongly alkaline reaction, and gives very characteristic reactions with solutions of metallic salts; on the addition of nickel sulphate, for example, there is obtained a yellow solution from which well-defined, yellow crystals are deposited on evaporation; cobalt nitrate produces a reddish-brown, and ferric chloride a yellowish-brown coloration. When aqueous solutions of equal quantities of the base and of copper sulphate are mixed, a dark, reddish-violet coloration is produced, and, on evaporating the solution, dark-violet crystals, which are very readily soluble in water but insoluble in alcohol and ether, are deposited. The compound $(C_5H_{12}N_2O)_2,AgNO_3$ is precipitated on adding a concentrated solution of silver nitrate to an aqueous solution of the base; it melts and takes fire when heated strongly, and rapidly darkens on exposure to the air. The *hydro-*

chloride, $C_5H_{12}N_2O,HCl$, separates from alcohol in deliquescent crystals, is very readily soluble in water, and melts at 186—187° with decomposition; the vapours evolved on heating the salt impart a red colour to a pine-chip moistened with hydrochloric acid.

Dibenzoylamylenenitrolamine, $NHBz\cdot CMe_2\cdot CMe\colon N\cdot OBz$, prepared by shaking the base with potash and benzoic chloride, crystallises well from ethyl acetate, melts at 142—143°, and is readily soluble in ether, but only sparingly in cold alcohol, and insoluble in water and alkalis. The *benzoyl* derivative, $NHBz\cdot CMe_2\cdot CMe\colon NOH$, is formed when the dibenzoyl derivative (5 grams) is boiled with an alcoholic solution of potash (0·86 gram) for an hour; it crystallises from boiling alcohol, melts at 184—185°, and is soluble in alkalis, but only very sparingly soluble in boiling water.

Benzoylamyleneketoamine, $NHBz\cdot CMe_2\cdot COMe$, is obtained when benzoylnitrolamine is boiled for a short time with dilute (1 : 19) sulphuric acid; it separates from alcohol in crystals, melts at 120—121°, and is readily soluble in alcohol and ether, but only sparingly in cold water, and insoluble in alkalis.

The *hydrazone*, $NHPh\cdot CMe_2\cdot CMe\colon N_2HPh$, is deposited in yellow crystals, when a concentrated aqueous solution of the ketoanilide $NHPh\cdot CMe_2\cdot COMe$, previously described (Abstr., 1888, 37), is treated with phenylhydrazine; it melts at 96—97°, and is insoluble in water, but readily soluble in ether and hot alcohol.

Amylenenitrol-α-naphthylamine, $C_{10}H_7\cdot NH\cdot CMe_2\cdot CMe\colon NOH$, can be obtained by boiling amylene nitrosate with an alcoholic solution of α-naphthylamine; it separates from boiling alcohol in well-defined, colourless crystals, melts at 173—174°, and is readily soluble in ether, but only sparingly in cold alcohol, and insoluble in water.

Amylenenitrolorthamidoquinoline, $C_9NH_7\cdot NH\cdot CMe_2\cdot CMe\colon NOH$, prepared in like manner, crystallises in reddish plates, melts at 153—154°, and is readily soluble in ether, but only sparingly in alcohol.

F. S. K.

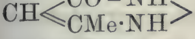
Decomposition of Amylene Nitrosate with Sodium Ethoxide. By O. WALLACH and P. ENGELS (*Annalen*, **262**, 339—354).—Three oximes having the empirical formula C_5H_9NO are formed when amylene nitrosate (32 grams) is added to a cool solution of sodium (4·6 grams) in absolute alcohol (120 c.c.) and the mixture warmed for a short time to complete the reaction. Water is then added, the precipitated oil separated, and the residual alcoholic solution submitted to distillation with steam; the distillate is saturated with sodium chloride, extracted with ether, the ether evaporated, and the residue mixed with the original oil. This product contains the three compounds, which are separated as follows:—The mixture is distilled with steam, when the α-oxime, together with small quantities of the β-compound, passes over first in an oily condition; the distillate is saturated with sodium chloride, extracted with ether, and the α-oxime isolated by fractional distillation under reduced pressure. After some time, crystals of the β-oxime begin to collect in the condenser, but, on further distillation, the oily distillate solidifies more slowly; at this stage the process is stopped and the oil in the residue is extracted with ether; on evaporating the ethereal solution, the γ-oxime is obtained in crystals together with an oily mixture of the α- and β-compounds.

The *α-oxime* crystallises in transparent, colourless plates, melts at 45°, boils at 83—84° (55 mm.) and is very readily soluble in ether, alcohol, benzene, chloroform, and light petroleum, but more sparingly in water; it dissolves in soda, yielding, under suitable conditions, a crystalline sodium derivative, and with hydrogen chloride in ethereal solution it gives a colourless precipitate. A vapour density determination by V. Meyer's method, and molecular weight determinations by Raoult's and by Raoult and Beckmann's methods, gave results agreeing with those required by a compound of the molecular formula C_5H_9NO. The *benzoyl* derivative, $C_5H_8\colon N\cdot OBz$, prepared by shaking an alkaline solution of the oxime with benzoic chloride, crystallises from dilute alcohol in lustrous needles and melts at 68—69°. The *dibromide*, $C_5H_9NOBr_2$, is formed when bromine is added to a well-cooled glacial acetic acid solution of the oxime until a permanent coloration is produced; it melts at 58°, and turns green when treated with soda, but the colour soon disappears again.

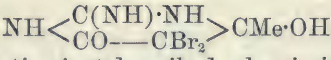
The *ketone*, C_5H_8O, is obtained when the oxime is heated with dilute sulphuric acid; it is an oil having an agreeable but rather pungent odour, and boils at 98—102°. It combines readily with bromine in ethereal or glacial acetic acid solution, and it is immediately oxidised by potassium permanganate; when treated with hydroxylamine, it is converted into the α-oxime (m. p. 45°).

The *β-oxime* is the principal product of the action of sodium ethoxide on amylene nitrosate; it separates from alcohol in well-defined, transparent crystals, melts at 67—68°, and boils at 129—134° under a pressure of 25 mm., and at 120—122° under a pressure of 11 mm.; it is insoluble in soda. Its molecular weight was determined by Raoult's methods and its vapour density by Meyer's method, employing the vapour of amyl acetate and of diphenylamine; the results showed beyond doubt that the compound has the molecular formula $C_{10}H_{18}N_2O_2$, but clearly indicated a dissociation of the molecule under the conditions of the experiment; the solid compound obtained by the condensation of the vapour of the β-oxime, which had been heated to the boiling point of diphenylamine, was found to be the α-oxime. The *dibromide*, $C_{10}H_{18}N_2O_2Br_2$, prepared by treating the β-oxime with bromine in glacial acetic acid solution, separates from dilute alcohol in crystals melting at 102°; when boiled with alcoholic potash, it loses 1 mol. of hydrogen bromide, and is converted into the *bromo*-derivative, $C_{10}H_{17}N_2O_2Br$, which crystallises in colourless prisms and melts at 87°.

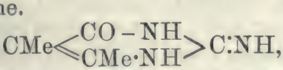
The *γ-oxime* crystallises from alcohol in colourless needles, melts at 111°, and is only moderately easily soluble in cold alcohol, and insoluble in water and alkalis. Molecular weight determinations by Raoult's method gave results agreeing with those required by a compound of the molecular formula $C_{15}H_{27}N_3O_3$, but the complex molecule easily undergoes dissociation on heating, the compound being converted into the α-oxime. The *dibromide*, $C_{15}H_{27}N_3O_3Br_2$, separates from dilute alcohol in crystals and melts at 82°; when heated for a short time with alcoholic potash, it is converted into the *bromo*-derivative, $C_{15}H_{26}N_3O_3Br$, which crystallises from alcohol in needles and melts at 102°. F. S. K.

Condensation of Guanidine with Ethereal Salts of β-Ketonic Acids. By J. JAEGER (*Annalen*, **262**, 365—372).—Imidomethyluracil,  $\mathrm{CH}{<}\begin{smallmatrix}\mathrm{CO-NH}\\ \mathrm{CMe{\cdot}NH}\end{smallmatrix}{>}\mathrm{C{:}NH}$, is deposited in crystals when guanidine carbonate (8 grams) is heated for four hours with an alcoholic solution of ethyl acetoacetate (12 grams) (compare Köhler, *Ber.*, **19**, 220). It crystallises in prisms, melts at 270° with decomposition, and is readily soluble in alkalis and hot water, but only sparingly in alcohol and cold water, and insoluble in ether. The *hydrochloride*, $C_5H_7N_3O,HCl$, forms long, colourless crystals and melts at 295°. The acid *sulphate*, $C_5H_7N_3O,H_2SO_4$, crystallises in small plates and melts at 180°. The *nitrate*, $C_5H_7N_3O,HNO_3$, crystallises from warm, dilute nitric acid in colourless, lustrous needles, explodes at 120°, and is decomposed by boiling water.

Bromimidomethyluracil, $C_5H_6BrN_3O$, is obtained when imidomethyluracil is treated with excess of anhydrous bromine; it is a yellowish powder, only very sparingly soluble in water, and when heated with concentrated ammonia at 200°, it is converted into an amido-compound which melts at 275°.

Dibromohydroxyimidomethyluracil,  $\mathrm{NH}{<}\begin{smallmatrix}\mathrm{C(NH){\cdot}NH}\\ \mathrm{CO{-\!-}CBr_2}\end{smallmatrix}{>}\mathrm{CMe{\cdot}OH}$, is formed, together with the bromo-derivative just described, when imidomethyluracil is suspended in water and bromine added until a permanent coloration is produced; it crystallises from water in colourless needles, melts at 160°, and is decomposed by boiling alcohol, being converted into bromimidomethyluracil.

A compound of the composition $(C_5H_6N_3OMe)_2,HI$ is obtained when imidomethyluracil is heated with excess of methyl iodide for some hours at 140°, the solution evaporated, and the residue recrystallised from hot water; it melts at 212°, and is decomposed by potassium carbonate yielding *methylimidouracil*, $C_5H_6N_3OMe$, which crystallises from hot water in long, lustrous prisms and melts at 312°. The *hydrochloride*, $C_5H_6N_3OMe,HCl + H_2O$, is a crystalline compound readily soluble in water. The *sulphate*, $(C_5H_6N_3OMe)_2,H_2SO_4$, is crystalline and melts at 270°. When methylimidomethyluracil is heated with a solution of barium hydroxide, it is decomposed with evolution of methylamine.

Imidodimethyluracil,  $\mathrm{CMe}{<}\begin{smallmatrix}\mathrm{CO-NH}\\ \mathrm{CMe{\cdot}NH}\end{smallmatrix}{>}\mathrm{C{:}NH}$, can be prepared by heating guanidine carbonate with an alcoholic solution of ethyl methylacetoacetate; it separates from alcohol in spherical aggregates, melts at 320°, and is almost insoluble in water, alcohol, and ether. The acid *sulphate*, $C_6H_9N_3O,H_2SO_4$, crystallises in small, colourless needles, and melts at 265°. The *nitrate*, $C_6H_9N_3O,HNO_3$, crystallises from warm dilute nitric acid in lustrous plates melting at 200°.

Imidophenyluracil, $C_{10}H_9N_3O$, prepared by treating guanidine carbonate with ethyl benzoylacetate, is an amorphous powder; it melts at

294°, and is insoluble in water, alcohol, and ether, but soluble in acids, forming salts. F. S. K.

"Rubeanic Acid." By O. WALLACH and G. REINHARDT (*Annalen*, **262**, 354—364).—The following experiments show that the red compound ("rubeanic acid, rubeanwasserstoff") obtained by the combination of cyanogen and hydrogen sulphide behaves in many reactions as if it were dithioxamide, $NH_2{\cdot}CS{\cdot}CS{\cdot}NH_2$ (compare Ephraim, this vol., p. 831); the sodium derivative, on the other hand, has doubtless the constitution $SNa{\cdot}C(NH){\cdot}C(NH){\cdot}SNa$ (compare Wallach, *Ber.*, **13**, 528).

Dibenzyldithioxamide, $C_7H_7{\cdot}NH{\cdot}CS{\cdot}CS{\cdot}NH{\cdot}C_7H_7$, is formed, with evolution of ammonia, when dithioxamide (rubeanic acid) is heated with benzylamine in alcoholic solution, and also when dibenzyloxamide (m. p. 219°) is melted with phosphorus pentasulphide; it separates from hot ethyl acetate in yellowish-red crystals, melts at 115°, and is only sparingly soluble in warm alcohol, but more readily in ether. It is insoluble in aqueous, but readily soluble in alcoholic potash, the salt thus obtained being decomposed by carbonic anhydride; its alcoholic solution gives precipitates with lead acetate and mercuric chloride.

Dimethyldithioxamide, $NHMe{\cdot}CS{\cdot}CS{\cdot}NHMe$, can be prepared by warming dithioxamide with methylamine in dilute alcoholic solution, and also by treating the compound $NHMe{\cdot}CCl_2{\cdot}CCl_2{\cdot}NHMe$ (compare Wallach and Pirath, *Ber.*, **12**, 1063) with hydrogen sulphide; it forms yellow crystals, melts at 140°, and is readily soluble in alkalis, but only sparingly in alcohol. When boiled with benzylamine, it is converted into dibenzyldithioxamide with evolution of methylamine.

Diethyldithioxamide, $NHEt{\cdot}CS{\cdot}CS{\cdot}NHEt$, prepared by analogous reactions, forms yellowish-red crystals, melts at 58°, and is readily soluble in alcohol, ether, benzene, and chloroform, but more sparingly in light petroleum, and almost insoluble in water; it dissolves freely in cold alkalis yielding compounds which are decomposed by carbonic anhydride.

Diamyldithioxamide, $C_5H_{11}{\cdot}NH{\cdot}CS{\cdot}CS{\cdot}NH{\cdot}C_5H_{11}$, prepared by warming dithioxamide with amylamine in alcoholic solution, crystallises in red prisms and melts at 60°.

Isodimethyldipropyldithioxamide, $SPr{\cdot}C(NMe){\cdot}C(NMe){\cdot}SPr$, can be obtained by boiling dimethyldithioxamide with sodium ethoxide (2 mols.) and propyl chloride (2 mols.) until the separation of sodium chloride is at an end; it is a yellowish oil.

Isotetrethyldithioxamide, $SEt{\cdot}C(NEt){\cdot}C(NEt){\cdot}SEt$, can be prepared from diethyldithioxamide and ethyl iodide in like manner; it is an oil. F. S. K.

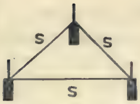
Isomerism of Thioaldehydes. By E. BAUMANN and E. FROMM (*Ber.*, **24**, 1419—1430; compare next abstract and p. 1050).—Formaldehyde and acetone each yield only one trithio-derivative; acetaldehyde and benzaldehyde, however, yield three, as will be shown later (this vol., pp. 1010 and 1050). Marckwald's γ-trithioacetaldehyde is merely impure α-trithioacetaldehyde. The compound at present termed α-trithiobenzaldehyde is in reality a polymeric derivative of high molecular weight, whilst the γ-trithiobenzaldehyde (m. p. 167°) of the authors, from its close analogy with α-trithioacetaldehyde, will in future be termed the α-form. The trithiobenzaldehydes, on heating with copper, are decomposed quantitatively into cinnamene, but this is no proof of their having the formula $CHPh<{}^{S}_{S}>CHPh$, since similarly constituted compounds, by simple heating, are converted into substances of lower molecular weight. It has also been shown that the formation of polymeric thioaldehydes, by the action of hydrogen sulphide on aldehydes in aqueous solution, is not direct, but is preceded by the formation of mercaptans or hydroxymercaptans; under the influence of condensing agents, these compounds then polymerise with elimination of hydrogen sulphide or water respectively.

Molecular weight determinations have proved that, by the interaction of hydrogen sulphide and aldehydes, in presence of hydrochloric acid, trithio-derivatives are exclusively formed, and that they exist in two isomeric modifications, the α- or lower melting isomerides are obtained in largest quantity at low temperatures, and are converted into the β-modifications by the action of iodine and similar substances; the more stable isomerides are formed in greatest proportion in excess of hydrochloric acid, and crystallise with 1 mol. benzene.

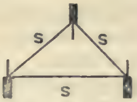
The researches of Klinger have shown that the trithiacetic aldehydes are substitution products of trithioformaldehyde (trithiomethylene), which has the formula $S<{}^{CH_2\cdot S}_{CH_2\cdot S}>CH_2$; the isomerism of the compounds is evidently geometric, and is not dependent on the sulphur atoms. These substances may therefore be regarded as affording the simplest example of isomerism, similar to that developed by v. Baeyer in the case of the hydrophthalic acids, and his system of nomenclature may be conveniently employed to distinguish the various modifications.

Mono-substitution derivatives of trimethylene or trithiomethylene can only exist in one form; di- and tri-substitution products may exist in two forms unless two substitution groups are linked to the same carbon atom; tetra-substituted derivatives resemble the di-substitution products; whilst penta- and hexa-derivatives are incapable of occurring in geometrically different forms. The foregoing applies only when the substituting groups are alike; if unlike, the number of isomerides is considerably increased.

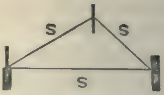
The following diagrams represent the possible forms of trisubstituted trithiomethylene; the present β-trithioaldehydes, being the more stable compounds are ranged in the trans- or fumaroïd class. The carbon atoms are assumed to occupy the corners of the triangle, the thin lines representing methylene hydrogen, the thick ones the substituting groups:—



α-Cis- or maleinoïd form.

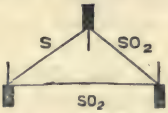


β-Trans- or fumaroïd form.

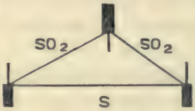


No isomerism.

Besides the difference in physical properties, the two forms may further be distinguished by the fact that, on oxidation, the cis-compound could only yield one disulphone sulphide, whilst the trans-derivative should give two, corresponding with the formulæ



&



respectively.

The following table shows all the trithioaldehydes at present known; those marked * are described for the first time by the authors in the following papers:—

Aldehyde.	α- or cis-form.	β- or trans-form.
Acetic	α-trithioacetaldehyde (m. p. 101°)	β-trithioacetaldehyde (m. p. 125°).
Benzoic	*α-trithiobenzaldehyde (m. p. 167°)	β-trithiobenzaldehyde (m. p. 225°).
Paramethoxybenzoic	*α-trithioparamethoxybenzaldehyde (m. p. 127°)	*β-trithioparamethoxybenzaldehyde (m. p. 183°).
Orthomethoxybenzoic.	*α-trithioethomethoxybenzaldehyde (m. p. 157°)	*β-trithiorthomethoxybenzaldehyde (m. p. 224°).
Orthisobutoxybenzoic.	*α-trithioethisobutoxybenzaldehyde (m. p. 142°)	*β-trithiorthisobutoxybenzaldehyde (m. p. 163°).
Cinnamic	*α-trithiocinnamaldehyde (m. p. 167°)	*β-trithiocinnamaldehyde (m. p. 213°).
Formic	trithiomethylene (m. p. 216°).	
Acetone	trithioacetone (m. p. 24°).	

J. B. T.

Trithio-derivatives of Acetaldehyde and Polymeric Thioformaldehyde. By E. BAUMANN and E. FROMM (*Ber.*, **24**, 1457—1469; compare preceding abstract).—Marckwald has stated that three products are formed on heating thialdine thiocyanate in aqueous solution; these are thiacetaldehyde, γ-trithiacetaldehyde, and a compound of the formula $NH{:}C{<}\substack{S\cdot CHMe \\ S\cdot CHMe}{>}S$. The authors have repeated this work, and have found that, during the decomposition of the thialdine salt, hydrogen sulphide is evolved. Marckwald's thiacetaldehyde contains ordinary aldehyde, and may be separated by treatment with water, which converts the thiacetaldehyde into a hydroxymercaptan; the constitution of this is uncertain, but it is undoubtedly a complicated polymeride of hydroxyethylidene mercaptan, $SH\cdot CH_2\cdot CH_2\cdot OH$.

On treatment of this compound with concentrated hydrochloric acid, α-trithiacetaldehyde is formed (m. p. 101—102°), instead of the γ-derivative, and is readily purified by crystallisation from acetone. Thiacetaldehyde, on treatment with hydrochloric acid, also yields α-trithiacetaldehyde, and not the γ-compound as stated by Marckwald. An examination of the second product (see above) obtained by the decomposition of thialdine thiocyanate shows that it is simply impure α-trithiacetaldehyde; three different preparations melted at 71—72°, 73—74°, and 76—77°, but, after recrystallisation from acetone, they all melted at 101°. The impurity, although sufficient to lower the melting point, does not affect the analytical results. A compound (m. p. 75—76°) prepared by Poleck and Thümmel by the action of hydrogen sulphide on vinylmercuric oxychloride in hydrochloric acid solution is also without doubt α-trithiacetaldehyde.

The polymeric thioformaldehyde of Wohl is insoluble in all menstrua, including naphthalene; it is not volatile with steam, decomposes on heating slightly above its melting point, and is oxidised with difficulty, yielding sulphuric acid and methylenedisulphonic acid. The trithioaldehydes of the aliphatic series are all converted on oxidation into disulphone sulphides or trisulphones. Wohl's substance is rather to be regarded as a complicated polymeric compound or as a mixture, since different preparations melt at various temperatures between 175° and 186°.

Trithiacetaldehyde is therefore proved only to exist in two forms, corresponding in this respect with the aromatic trithioaldehydes, whilst only one trithioformaldehyde is known. J. B. T.

Dimethylacrylic Acid from Isovaleric Acid. By E. DUVILLIER (*Compt. rend.*, **112**, 1012).—In the preparation of amido-acids from isovaleric acid, the yield was less satisfactory than in the case of normal butyric or propionic acids. It was thought that this was due to the formation of dimethylacrylic acid, as in the action of trimethylamine on ethyl bromisovalerate (Abstr., 1890, 956). Preparing the amide in the usual manner from isovaleric acid, before liberating the amido-acid, the liquid was distilled; the distillate yielded an oily liquid scarcely soluble in water, distilling at 175—195°, absorbing bromine and iodine, and partially crystallising. The crystals have the composition and properties of dimethylacrylic acid. The action of ammonia on normal α-bromo-acids has not given unsaturated acids. Ammonia, acting on bromisobutyric acid, yields an unsaturated acid, which is now under investigation. W. T.

Distillation of the Potassium Hydrogen Salts of some Acids of the Oxalic Series. By G. WISBAR (*Annalen*, **262**, 219—232).—It has been stated by Claus (*Annalen*, **191**, 48) that at a high temperature glutaric acid is decomposed into carbonic anhydride and butyric acid; the authors made a number of experiments under various conditions in order to ascertain whether both normal and isobutyric acid are formed on heating pure glutaric acid, but they were unable to detect the presence of either compound in the products of decomposition.

The behaviour of several potassium hydrogen salts, at a temperature of about 260°, was then investigated qualitatively and quantitatively, the dry salt being heated in a glass distilling flask in the vapour of amyl benzoate, and the gaseous and liquid products collected.

Anhydrous potassium hydrogen oxalate is quickly decomposed into potassium oxalate, water, formic acid, carbonic oxide, and carbonic anhydride.

Anhydrous potassium hydrogen malonate is also quickly decomposed, the principal products being potassium acetate and carbonic anhydride, but a small quantity undergoes decomposition into potassium malonate, acetic acid, and carbonic anhydride.

Potassium hydrogen succinate is much more slowly decomposed, yielding carbonic anhydride, an aqueous and an oily distillate, and non-volatile compounds. When the distillate is boiled with water, a very small quantity of an acid, probably propionic acid, passes over, together with a brown, neutral oil, which has approximately the composition $C_{10}H_{14}O$, and a little succinic acid remains in solution. The non-volatile residue contains potassium succinate and one or more acid subtances of high molecular weight.

One of these acids can be isolated by extracting the residue with boiling alcohol, evaporating the cold, filtered solution, dissolving the residue in sodium carbonate, and then acidifying with hydrochloric acid, when it is deposited in the form of an amorphous, light-coloured precipitate; it is dissolved in alcohol, fractionally precipitated from the solution with light petroleum, dissolved in ammonia, and then reprecipitated with hydrochloric acid. It is thus obtained in the form of a brownish, amorphous powder, which has the composition $C_{26}H_{30}O_5$, is insoluble in water, and decomposes on heating; the silver salt, $C_{26}H_{29}AgO_5$, is a reddish-brown, jelly-like substance. The portion of the original residue which is not dissolved by the boiling alcohol also contains amorphous substances of high molecular weight, two of which were isolated and analysed; the one gave results agreeing with those required by a compound of the composition $C_{26}H_{30}O_6$ or $C_{26}H_{32}O_6$, and had an acid character; the other is a brown powder, insoluble in alkalis, the composition of which may be represented by the formula $C_{27}H_{30}O_5$.

Potassium hydrogen glutarate is decomposed at 260° with evolution of carbonic anhydride; the distillate contains only traces of a volatile acid, and the residue consists of potassium glutarate and dark, acid, condensation products. F. S. K.

Ethyl Hydrogen Malonate and Ethyl Potassium Malonate. By G. MASSOL (*Compt. rend.*, **112**, 734—735).—Ethyl hydrogen malonate is obtained by adding to ethyl potassium malonate the calculated quantity of sulphuric acid, evaporating in a vacuum in presence of sulphuric acid, and extracting with ether. The ethereal solution is first distilled, and afterwards allowed to evaporate spontaneously. Ethyl hydrogen malonate is left as a slightly viscous liquid with a feeble, aromatic odour; sp. gr. at 0° = 1·201; refractive index at 22°, for white light = 1·333, for D = 1·337; heat of dissolution +0·60 Cal.; heat of neutralisation by potash +13·45 Cal., a number practically the same as the heat of neutralisation of potassium hydrogen malonate.

Potassium ethyl malonate is obtained in colourless lamellæ, very soluble in water, by evaporating a solution of ethyl hydrogen malonate that has been exactly neutralised with potash. Heat of dissolution, −0·65, and hence $C_3H_3EtO_4$ liq. + KOH sol. = $C_3H_2O_4KEt$ sol. + H_2O sol. develops + 28·6 Cal., a number practically identical with the heat of formation of hydrogen potassium malonate, +27·5 Cal., but distinctly greater than the heat of formation of normal potassium malonate from hydrogen potassium malonate, +20·7 Cal.

C. H. B.

Decomposition of Glutaric Acid and Succinic Acid by Sunlight in Presence of a Uranium Salt. By G. WISBAR (*Annalen*, **262**, 232—236).—According to Seekamp (*Annalen*, **133**, 254), an aqueous solution of glutaric acid undergoes decomposition in sunlight in presence of a uranyl salt, with formation of butyric acid and evolution of carbonic anhydride. The authors have investigated this reaction more closely, and find that normal butyric acid, but no isobutyric acid, is formed, with evolution of carbonic anhydride and small quantities of propane; the last-named compound is produced by the decomposition of some of the butyric acid in presence of sunlight and uranyl nitrate.

F. S. K.

Hydrolysis of Ethereal Salts of Polybasic Acids. By W. LOSSEN and A. KÖHLER (*Annalen*, **262**, 196—219).—The following experiments were made with the object of ascertaining whether the course of hydrolysis of a mixed ethereal salt, such as methyl ethyl succinate, is dependent on the nature of the alcohol radicles, and also, whether in the case of such ethereal salts as methyl ethyl glutarate, of which there exist theoretically two isomerides, the course of hydrolysis is determined by the nature of the alcohol radicle, as well as by the structure of the molecule.

The method of preparation of many of the ethereal salts which were examined in this research has been previously described by Wiens (Abstr., 1890, 102).

When methyl ethyl succinate (45 grams, 2 mols.) is shaken with a solution of barium hydroxide (43 grams, 1 mol.) in water (1 litre) until the reaction is complete, barium succinate (15·2 grams) is formed by the complete hydrolysis of a portion (9·6 grams) of the ethereal salt, but an equal quantity (9·6 grams) remains undecomposed, and a large quantity (about 26 grams) is converted into a mixture of ethyl and methyl barium succinates, of which the former is present in the larger proportion; a quantitative examination showed that methyl and ethyl alcohols were liberated in the hydrolysis in the molecular proportion 100 : 72, approximately.

When ethyl propyl succinate (47 grams, 2 mols.) is treated in like manner with a solution of barium hydroxide (38·3 grams, 1 mol.) in water (1 litre), about one-half of the ethereal salt is completely converted into barium succinate, the remainder being undecomposed; when a more dilute solution of barium hydroxide is employed, a considerable quantity of a mixture of ethyl and propyl barium succinate is also formed.

It has been observed by Salomon (*Ber.*, **8**, 1508) that methyl potassium oxalate is formed on treating ethyl oxalate with a methyl alcoholic solution of potassium methoxide; the authors find that an analogous reaction takes place in the case of other oxalates. Propyl oxalate, for example, is converted into methyl potassium oxalate by an anhydrous methyl alcoholic solution of potassium methoxide, and into ethyl potassium oxalate by an ethyl alcoholic solution of potassium ethoxide. When ethyl oxalate is treated with a solution of potassium propoxide in propyl alcohol, propyl potassium oxalate is formed; methyl oxalate is converted into ethyl potassium oxalate by an alcoholic solution of potassium ethoxide, and when treated with a solution of potassium in propyl alcohol, it yields propyl potassium oxalate. Such reactions as these, taking place as they do in presence of excess of a particular alcohol, may be modified considerably by changing the conditions, as is shown by the following facts:—(1.) When propyl oxalate is treated with a methyl alcoholic solution of potassium methoxide mixed with three volumes of propyl alcohol, a mixture of methyl and propyl potassium oxalate is deposited. (2.) On treating a mixture of propyl alcohol and propyl oxalate with an alcoholic solution of potassium ethoxide, both propyl and ethyl potassium oxalates are formed; if, on the other hand, a mixture of methyl alcohol and methyl oxalate is treated with a solution of potassium propoxide in propyl alcohol, methyl potassium oxalate is deposited in an almost pure condition. (3.) When excess of ethyl oxalate is treated with a small quantity of a methyl alcoholic solution of potassium methoxide, the principal product is ethyl potassium oxalate.

When ethyl oxalate is treated with anhydrous potassium ethoxide, a small quantity of a liquid, having the properties of ethyl ether, is obtained; it would seem therefore that the formation of the alkyl potassium oxalate in the reactions described above may be expressed by the equation $C_2O_4Et_2 + KOEt = C_2O_4EtK + Et_2O$.

When ethyl propyl oxalate is treated with phosphorus pentachloride, both ethyl chloride and propyl chloride are evolved, and there remains a mixture of the chlorides of ethyl hydrogen and propyl hydrogen oxalate.

Methyl carbonate is decomposed by an alcoholic solution of potassium ethoxide, yielding a mixture of methyl and ethyl potassium carbonates; under the same conditions, ethyl glutarate yields small quantities of ethyl potassium glutarate, and a large quantity of potassium glutarate; when methyl glutarate is treated with barium methoxide, barium glutarate is formed in large quantities, together with the barium methyl salt.

Ethyl dihydrogen phosphate can be obtained by decomposing the barium ethyl salt, $BaEtPO_4 + 6H_2O$, with the theoretical quantity of dilute sulphuric acid, and evaporating the filtered solution; it is a very deliquescent, readily fusible, crystalline compound.

Barium diethyl phosphate is easily prepared by decomposing triethyl phosphate with an aqueous solution of barium hydroxide, and evaporating the filtered solution; the free acid could not be obtained in crystals, but the *silver* salt, $AgEt_2PO_4$, crystallises in needles.

Methyl silver phosphate is a colourless, crystalline compound sparingly soluble in water.

Barium dimethyl phosphate, $(Me_2PO_4)_2Ba$, prepared from the trimethyl salt, is readily soluble in water, but is precipitated from the solution on the addition of alcohol; the corresponding *silver* salt, $AgMe_2PO_4$, crystallises from water, in which it is readily soluble, in plates.

Dibenzyl hydrogen phosphate, $(C_7H_7)_2HPO_4$, can be prepared by shaking tribenzyl phosphate with hot, very concentrated potash, and decomposing the potassium salt obtained in this way with hydrochloric acid; it crystallises in needles or prisms, melts at 78—79°, and is readily soluble in alcohol and ether, but only sparingly in water. The *calcium* salt, $[(C_7H_7)_2PO_4]_2Ca + 6H_2O$, and the *barium* salt are crystalline, and soluble in hot water, but the *silver* salt is only sparingly soluble. The normal salts of dibenzyl hydrogen phosphate are very stable; potassium dibenzyl phosphate, for example, is not decomposed even on prolonged heating with excess of concentrated potash.

Tribenzyl phosphate, $(C_7H_7)_3PO_4$, is prepared by warming silver phosphate with an ethereal solution of benzyl chloride; it forms large, prismatic crystals, melts at 64°, and is soluble in the ordinary organic solvents, but insoluble in water.

Ethyl dimethyl phosphate, $EtMe_2PO_4$, can be obtained by treating ethyl disilver phosphate with methyl iodide, or by treating silver dimethyl phosphate with ethyl iodide; it boils at 203·3°, and its specific gravity is 1·1752 at 0°. On hydrolysis with an aqueous solution of barium hydroxide, it is easily converted into barium ethyl methyl phosphate with liberation of methyl alcohol; ethyl methyl hydrogen phosphate is, however, a very stable compound, and is not decomposed by bases, so that it would seem from these facts that one of the alkyl groups in the normal ethereal salts is combined differently to the others.

Methyl diethyl phosphate, $MeEt_2PO_4$, prepared from methyl disilver phosphate, or from silver diethyl phosphate, is a colourless liquid of sp. gr. 1·1282 at 0°, and boils at 208·2° under a pressure of 759·7 mm.; on hydrolysis with a solution of barium hydroxide, it yields methyl ethyl barium phosphate.

Methyl dibenzyl phosphate, $Me(C_7H_7)_2PO_4$, is formed when an ethereal solution of benzyl chloride is warmed with methyl disilver phosphate, and when silver dibenzyl phosphate is treated with methyl iodide; it is a brownish oil of sp. gr. 1·2005 at 0°, and cannot be distilled. It is much more difficult to hydrolyse than the ethereal salts described above, but when shaken with hot, very concentrated potash, it is converted into potassium dibenzyl phosphate. F. S. K.

Symmetrical Dimethylglutaric Acid and Trimethylsuccinic Acid. By K. AUWERS and E. KÖBNER (*Ber.*, **24**, 1923—1937).—The authors have determined the nature of the acid obtained by the action of α-bromisobutyric acid on ethyl sodium methylmalonate and hydrolysis of the product by boiling with acids, concerning which acid many different opinions have been put forward. They find that this acid is identical with the symmetrical dimethylglutaric acid (m. p. 102—104°) which Zelinsky (Abstr., 1890, 132) has prepared from ethyl α-cyanopropionate and methylene iodide. They have prepared some quantity of the acid from α-bromisobutyric acid and ethyl sodium methylmalonate. It melts at 102—103°, yields an anhydride melting at 95°, and the latter, when boiled with water, is converted to an acid which melts at 127·5—128°. Both these acids yield the same anhydride. By heating the acid melting at 127—128° with hydrochloric acid at 200°, it is converted into the acid melting at 102—103°. These results leave no doubt that the acid is dimethylglutaric acid. Auwers and Jackson (Abstr., 1890, 1098) have put forward an explanation of the above reaction. They assume that in the presence of an alcoholic alkaline solution, the α-bromisobutyric acid is converted into methylacrylic acid, and that the latter condenses with the ethyl sodium methylmalonate to yield a product which, on hydrolysis, gives dimethylglutaric acid. The authors have obtained dimethylglutaric acid from methylacrylic acid. An analogous reaction takes place between ethereal salts of crotonic acid and ethyl sodium malonate when β-methylglutaric acid is formed instead of ethylsuccinic acid.

Symmetrical dimethylglutaric acid (m. p. 102—103°) is best prepared as follows:—Ethyl α-bromisobutyrate (195 grams) is warmed on the water-bath and added to a hot, alcoholic solution of ethyl methylmalonate (170 grams) and sodium (22·5 grams); a brisk reaction takes place; the mixture is digested on the water-bath for five hours, and the alcohol distilled off. The ethyl tricarboxylate so obtained is hydrolysed by heating with concentrated hydrochloric acid ($\frac{3}{4}$ vol.) and water ($\frac{3}{4}$ vol.). On cooling, the acid separates in pure white, prismatic crystals, and is purified by crystallisation from benzene, and finally by dissolution in chloroform and fractional precipitation with light petroleum. It melts at 102—103°, crystallises in small, shining prisms, and is easily soluble in water, chloroform, ether, alcohol, and acetic acid, sparingly in cold benzene, and insoluble in light petroleum. The *anhydride* is obtained by digesting the acid with acetic chloride on the water-bath, or by heating it in a sealed tube with acetic chloride at 100°. It crystallises from light petroleum in feathery needles, and melts at 95°. When the acid is heated for some time at 200° and the product distilled, washed with soda, and crystallised from petroleum, a substance is obtained which melts at 82—83°; this the authors believe is a mixture of the anhydrides of the two isomeric dimethylglutaric acids.

Dimethylglutaric acid (m. p. 127·5—128°) is obtained by boiling the above anhydride (m. p. 95°) with a little water. It crystallises in long, lustrous needles, melts at 127·5—128°, and is crystallographically identical with Zelinsky's high-melting dimethylglutaric acid. When heated with acetic chloride, it yields the same anhydride as the low-melting acid, and when heated with concentrated hydrochloric acid for 18 hours at 200°, it is converted into the low-melting acid.

The above acids have also been prepared from methylacrylic acid. *Ethyl methylacrylate* is prepared by digesting silver methylacrylate, ether, and ethyl iodide for six hours in a reflux apparatus, and is purified by fractional distillation. It boils at 115—120°, and has a strong, pleasant odour. Dimethylglutaric acid (m. p. 102—103°) is obtained when ethyl methylacrylate (15 grams) is added to a warm solution of ethyl methylmalonate (23 grams) and sodium (3 grams) in absolute alcohol, and the mixture heated for five hours on the water-bath. The product is purified by fractional distillation, and hydrolysed with hydrochloric acid. E. C. R.

Methyl Methylcyanosuccinate; Methyl Methylethenyltricarboxylate. By L. BARTHE (*Compt. rend.*, **112**, 1013—1015).—In a previous communication, it has been shown that methyl cyanosuccinate is obtained by treating methyl sodiocyanacetate with methyl monochloracetate (this vol., p. 43). This substance reacts readily, and it is easy to prepare its substitution derivatives.

Methyl methylcyanosuccinate, $COOMe{\cdot}CMe(CN){\cdot}CH_2{\cdot}COOMe$, is prepared by dissolving 20 grams of methyl cyanosuccinate in 60 grams of methyl alcohol and adding a solution of 2·38 grams of sodium in 100 grams of methyl alcohol; to this mixture is added 16·6 grams of methyl iodide rectified at 43°, and the whole is heated on a water-bath in a reflux apparatus for five hours. The temperature should be kept at from 70—75°. The precipitated sodium iodide is filtered off, and the alcohol separated by distillation. A reddish oil is precipitated from the residue by water and taken up by ether. The ethereal solution, dried by calcium chloride, is then distilled on the water-bath, and finally, under reduced pressure, on the oil-bath, when the methyl salt passes over at 195—200° (60 mm.) as an oily, colourless liquid. The same compound is formed in attempting to produce ethyl methylcyanosuccinate, if methyl alcohol be employed as the solvent. The author has not succeeded in obtaining methyl ethyl cyanosuccinate.

Methyl methylethenyltricarboxylate, $COOMe{\cdot}CH_2{\cdot}CMe(COOMe)_2$.—The above compound has been saponified by treatment with methyl alcohol saturated with hydrochloric acid, in sealed tubes at 75°, for one or two hours. The reaction does not take place in the cold, even after a long time. The liquid is evaporated on the water-bath, and then washed with sodium carbonate solution. The oily substance precipitated is taken up with ether, dried by calcium chloride, and distilled under reduced pressure. The greater part of the product distils over at 217° under 0·05 atmos. pressure. The properties of methyl cyanosuccinate and its substitution derivatives resemble those of ethyl cyanosuccinate and its derivatives. Other new compounds obtained with ethereal cyanacetates and cyanosuccinates will be described in a succeeding communication. W. T.

Isomeric Pimelic Acid from Amylene Bromide. By C. HELL (*Ber.*, **24**, 1389—1399).—Amylene bromide is boiled for 70 hours with an alcoholic solution of potassium cyanide; the product is hydrolysed, and the resulting acid crystallised from petroleum; it melts at 104°. During the purification a viscid liquid is obtained in small quantity, which Bauer and Schuler supposed to be an isomeric amorphous pimelic acid, but which crystallises on exposure in thin films, and proves to be identical with the chief product. The yield is 5 grams from 2 kilos. of amylene bromide. The salts are generally crystalline; the anhydrous *nickel salt* is yellow; two greenish-yellow salts are also formed, containing 1 mol. H_2O and $2\frac{1}{2}$ mols. H_2O respectively. On heating the acid at 135°, water is eliminated, and the *anhydride* is obtained; it is a viscid liquid, boiling above 200° without decomposition. Acetic acid is the sole oxidation product of the acid. It is probable that this acid is unsymmetrical ethylmethylsuccinic acid, and that its formation is due to the presence of a little ethylmethylethylene bromide in the amylene bromide, the bulk of which certainly consisted of trimethylethylene bromide, since the amylene employed for its preparation boiled at 35—38°; this would account for the exceedingly small yield. The absence of propionic acid in the oxidation products of the acid was the chief reason for the author's previously suggesting that it might be trimethylsuccinic acid.

The paper closes with some observations in reply to a recent paper of Zelinsky and Besredka (this vol., p. 669). J. B. T.

Preparation of Glyceryl Pyruvate. By C. Böttinger (*Annalen*, **263**, 246—247).—Glyceryl pyruvate, previously known as pyruvin or glycuvic acid, can be very easily prepared by heating finely-divided potassium hydrogen sulphate (5 grams) with pyruvic acid (2·5 c.c.) and glycerol (2·5 c.c.) for a short time over a small flame. The product is extracted with ether, the extract evaporated, and the thick, colourless syrup obtained in this way agitated with an equal volume of water, when pure glyceryl pyruvate is quickly deposited in lustrous plates. The portion insoluble in ether is extracted with boiling alcohol, the solution concentrated by evaporation, mixed with water, and extracted with ether; the residue obtained on evaporating the ether is then treated with an equal volume of water, when a second crop of crystals of glyceryl pyruvate is obtained.

F. S. K.

Constitution of Aqueous Solutions of Tartaric Acid. By Aignan (*Compt. rend.*, **112**, 951—953).—The results of Biot's observations on the rotatory power of aqueous solutions of tartaric acid may be explained on the assumption either that tartaric acid forms in solution a definite hydrate, which exists in a partially dissociated condition, or that the physical molecule is double the chemical molecule, but is likewise partially dissociated in solution. If the first assumption is true, Biot's results show that the proportion of tartaric acid which combines in a fixed ratio with *n* molecules of water in the form of non-dissociated hydrate is equal to the proportion of water in the solution, and in this case the osmotic pressure will be

$$\pi_1 = \mathrm{RT}\frac{\delta}{150}\epsilon.$$

In the second case, the results show that the proportion of the compound $(C_4H_6O_6)_2$ dissociated by dissolution is equal to the proportion of the solvent in the liquid examined; or, the weight of the active compound $(C_4H_6O_6)_2$ dissociated by dissolution is equal to the product of the weight of the solvent by the concentration ϵ of the solution, and the osmotic pressure will be

$$\pi_2 = \mathrm{RT}\,\frac{\delta}{150}\left(\epsilon - \frac{\epsilon^2}{2}\right).$$

A solution of tartaric acid containing 49·47 grams per kilogram (sp. gr. = 1·02241) is isotonic with a solution of sugar containing 112·47 grams per litre, and hence tartaric acid exists in solution in the form of the polymeride, $(C_4H_6O_6)_2$, which is partially dissociated, in accordance with the law already stated. C. H. B.

Combinations of Tartaric Acid and Potash, or Soda, in Solution. By AIGNAN (*Compt. rend.*, **112**, 1009—1011).—From the observation of the rotation of the plane of polarisation ω, given by a column of solution of length l, the quantity $[\omega] = \mathrm{M}\omega/\mathrm{P}l\delta$, where M = mass of solution containing a weight P of the active substance, δ = the specific gravity of the solution, was calculated by Biot for solutions containing tartaric acid mixed with various amounts of potash or soda respectively. He found the values of $[\omega]$ obtained to be represented graphically by an equilateral hyperbola, and concluded that combinations were formed in the solutions examined in continuously varying quantities (*Mém. Inst France*, **16**).

According to the author's theory, the line representing the values of $[\omega]$ should consist of arcs of curves crossing in angular points. To verify this conjecture, a series of observations have been taken sufficiently numerous to afford many more points than Biot obtained. The solutions used contained 150 grams, or one molecular weight of tartaric acid, with a proportion of soda varying from 0 to 22/5 of an equivalent in a mass $\mathrm{M} = 4000$ grams.

As tartaric acid forms, with potash and soda, 1st, an acid tartrate, 2nd, a normal tartrate, two angular points could be predicted; the author finds, on plotting out his results with weights of soda along x as abscissæ—

(1.) For varying quantities of soda from 0 to 1 equivalent, $[\omega]$ is represented by a curve which departs but little from a right line, and is convex towards the axis of x.

(2.) Between 1 and 2 equivalents, $[\omega]$ is represented by a right line, cutting the first arc of the curve at an open angle. This angular point indicates the formation of sodium hydrogen tartrate, as predicted.

(3.) From 2 to 3 equivalents, the curve is of different character, and clearly cuts the preceding at the point corresponding with the formation of the normal tartrate. This arc shows that $[\omega]$ attains a maximum value at about 11/5 equivalents of soda, and then decreases slowly.

(4.) At 3 equivalents, a third angular point occurs, indicating that further combination of the soda and tartaric acid takes place, then $[\omega]$ again increases slightly, and finally decreases slowly, apparently to a limiting value.

The existence of a third compound might have been foreseen, as Berthelot found the third equivalent of soda, added to tartaric acid, liberated 0·3 Cal. It is probably a true alcoholate, and from the author's observations partially dissociates in solution. W. T.

Formation of Inactive Tartaric Acid by the Oxidation of Phenol with Potassium Permanganate. By O. DOEBNER (*Ber*, **24**, 1753—1757).—Kekulé and Anschütz have shown that when fumaric acid is oxidised with potassium permanganate, racemic acid is formed, whilst maleïc acid yields inactive tartaric acid under the same circumstances. It would, therefore, appear that the carbon chain in inactive tartaric acid has the same stereochemical structure as that of maleïc acid, and as, further, the chain :CH·CH:CH·CH:, which exists in benzene, according to Kekulé's configuration, stands in stereochemical relation to the generally accepted formula for maleïc acid, it was to be expected that inactive tartaric acid would be formed by oxidising benzene with alkaline potassium permanganate; experiments proved, however, that the two are almost without action, and the author, therefore, substituted phenol for benzene with the following results:—Phenol (10 grams) is neutralised with a solution of sodium hydroxide, and the solution diluted with water to 1 litre; it is then cooled to 0—3°, and potassium permanganate (40 grams), in water (3 litres), gradually added. After several hours, the mixture is filtered from manganese dioxide; on adding an excess of hydrochloric acid to the filtrates from several experiments, and concentrating, a brownish-yellow, amorphous substance separates, which is filtered off. On treating the hot filtrate with calcium carbonate, and subsequently reacidifying with acetic acid, calcium oxalate remains undissolved, and the calcium salt of inactive tartaric acid separates from the filtrate; it is purified by dissolving in very dilute hydrochloric acid, adding ammonia, and then an excess of hot acetic acid; 90 grams of phenol yield calcium tartrate (9 grams), and oxalate (24 grams), besides carbonic anhydride. The production of inactive tartaric acid from phenol is, therefore, best explained by Kekulé's benzene formula, and the last-mentioned chemist has already shown (Abstr., 1884, 41) that tetrahydroxysuccinic acid is obtained by the oxidation of catechol with nitrous acid. Experiments are in progress with other benzene derivatives. A. R. L.

Substitution of Halogens in Aromatic Hydrocarbons. By G. ERRERA (*Gazzetta*, **21**, 103—110).—The author compares the results previously obtained by himself (Abstr., 1887, 1103) with Srpek's conclusions (this vol., p. 44) as to the constitution of the products of the bromination of benzyl chloride, and of the chlorination of parabromotoluene. The author maintains that the solid products consist mainly of a mixture of chloride and bromide of parabromobenzyl, and contain no chlorine in the nucleus.

S. B. A. A.

Action of Chromyl Dichloride on Cymene. By G. ERRERA (*Gazzetta*, **21**, 76—94).—*Paramethylhydratropaldehyde*,

$$C_6H_4Me·CHMe·CHO\ [1:4],$$

prepared by the action of chromyl dichloride on cymene (Abstr., 1884, 1342) and purified by combination with sodium hydrogen sulphite, is a liquid which boils at 233—234° and, according to the author, does not crystallise even after several months exposure to the air. The *aldoxime*, $C_6H_4Me{\cdot}CHMe{\cdot}CH{:}NOH$, is a heavy, colourless, uncrystallisable liquid insoluble in water.

Paramethylhydratroponitrile, $C_6H_4Me{\cdot}CHMe{\cdot}CN$, is readily obtained by the action of acetic anhydride on the aldoxime. It is a light, colourless liquid with a pleasant odour; it boils at 246·5—247·5° and is insoluble in water.

Paramethylhydratropic acid, prepared by Miller and Röhde (Abstr., 1890, 978) by the direct oxidation of the aldehyde, may also be obtained by boiling the preceding compound with aqueous potash. It melts at 40—41°, boils at about 280°, and yields a barium salt very soluble in water.

α-Methylhomoterephthalic acid, $COOH{\cdot}C_6H_4{\cdot}CHMe{\cdot}COOH$, is formed, together with terephthalic acid, when paramethylhydratropic acid is oxidised in alkaline solution with potassium permaganate. When pure, it crystallises in colourless, silvery plates, melts at 222—223°, dissolves sparingly in water and more freely in alcohol, but is insoluble in benzene and light petroleum. The *barium* salt is very soluble in water; the *lead* salt is almost insoluble; the *methyl* derivative, $C_{10}H_8O_4Me_2$, is a liquid insoluble in water and has a pleasant odour resembling methyl paratoluate. The *amide*,

$$CONH_2{\cdot}C_6H_4{\cdot}CHMe{\cdot}CONH_2,$$

crystallises in brilliant plates, melts at 227—229°, dissolves readily in boiling water and alcohol, but is sparingly soluble in the cold.

Paramethylhydratropyl alcohol, $C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}OH$ [1 : 4], is obtained by reducing a dilute alcoholic solution of the aldehyde with sodium amalgam. It is a light liquid with a pleasant odour, boiling at 239° and very sparingly soluble in water. The *acetate* is a colourless liquid with a fruity odour, which boils at 242—244° and is insoluble in water. The *chloride*, $C_6H_4Me{\cdot}CHMe{\cdot}CH_2Cl$, boils at 228° with partial decomposition, and is also insoluble in water.

β-Paratolylpropylene, $C_6H_4Me{\cdot}CMe{:}CH_2$, prepared by boiling the preceding compound with alcoholic potash, is a light, colourless, aromatic liquid which boils at 198—200° and is insoluble in water. It yields a liquid uncrystallisable additive compound with bromine, but, unlike α-paratolylpropylene, $C_6H_4Me{\cdot}CH{:}CHMe$ (Abstr., 1885, 654 and 772), it does not yield a solid polymeride on contact with calcium chloride.

The product of the action of chromyl chloride on cymene contains, besides paramethylhydratropaldehyde, a mixture of substances which do not combine with sodium hydrogen sulphite, and from which by repeated crystallisation, a compound identical with paratolylmethylketone, $C_6H_4Me{\cdot}COMe$ (Abstr., 1882, 970), may be isolated. The *metanitro-derivative* of this ketone [$COMe : NO_2 : Me = 1 : 3 : 4$], obtained by dissolving it in strongly cooled nitric acid (sp. gr. = 1·51), crystallises in long, yellow needles when pure, melts at 61°, and dissolves freely in alcohol. It combines with phenylhydrazine, and the product crystallises from alcohol in garnet-red prisms having a

composition corresponding with the formula $NO_2\cdot C_6H_3Me\cdot CMe\!:\!N_2HPh$. On oxidation with nitric acid, the nitroketone yields metanitroparatoluic acid.
S. B. A. A.

Synthesis of Parapropyltoluene and Parisopropyltoluene. By A. Töhl (*Ber.*, **24**, 1649—1653).—The author has repeated some of Widman's work on parapropyltoluene (this vol., p. 686) in the hope of reconciling the differences between his results and the earlier ones of Jacobsen. Parapropyltoluene from parabromotoluene and propyl bromide yields two barium salts; the yield of hydrocarbon is 32 per cent. Widman's conclusions are thus confirmed.

Parapropyltoluene from parabromotoluene and propyl iodide is identical with the preceding compound, and boils at 183—184°, instead of 175—176° as stated by Jacobsen; the yield is nearly 8 per cent. The purification of the hydrocarbon is a matter of extreme difficulty, and this probably accounts for Jacobsen's error in regard to the barium sulphonate.

Parisopropyltoluene from parabromisopropylbenzene and methyl iodide agrees in its properties with Widman's description.
J. B. T.

Paradipropylbenzene. By M. Fileti (*Gazzetta*, **21**, 22—28).—*Paradipropylbenzene* is best prepared by the action of metallic sodium on a mixture of parabromopropylbenzene and propyl bromide in ethereal solution in a manner analogous to that employed for the preparation of propylisopropylbenzene (see next abstract). The yield is 60 per cent. It boils at 220—221° (mercury column in the vapour) under a pressure of 745 mm. By oxidising paradipropylbenzene with dilute nitric acid, Körner (Abstr., 1883, 321) found that parapropylbenzoic acid is formed. In addition to this acid, the author has isolated from the products of oxidation terephthalic acid, an azotised compound which melts at 172° and crystallises from alcohol in slender, yellowish needles, and a small quantity of a substance melting at 79°.

Dinitrodibromoparadipropylbenzene crystallises from light petroleum in colourless or pale-yellowish, oblique prisms, melts at 145°, and dissolves freely in benzene, chloroform, and carbon bisulphide, moderately in ether, and sparingly in alcohol.

α-Diparapropylbenzenesulphonic acid was the only sulphonic acid isolated by Körner (*loc. cit.*) from diparapropylbenzene; the *barium* salt appears to contain 1 mol. H_2O; the *magnesium* salt $(C_{12}H_{17}SO_3)_2Mg,7H_2O$, crystallises in long plates or tabular prisms, and dissolves readily in boiling water; the *zinc* salt $(C_{12}H_{17}SO_3)_2Zn,8H_2O$, resembles the magnesium salt. The amide already prepared by Remsen and Keiser (Abstr., 1884, 457) crystallises from carbon bisulphide in brilliant, well-defined rhombohedra.

β-Diparapropylbenzenesulphonic acid.—Small quantities of this acid are obtained in the preparation of the α-acid, and may be separated from it by taking advantage of the greater solubility of the β-lead salt. The *amide* crystallises from carbon bisulphide in orthogonal, nacreous plates, melts at 106—107°, dissolves readily in alcohol, ether, &c., but not at all in water.

The corresponding sulphonic salts of dipropylbenzene and of propylisopropylbenzene exhibit very marked analogies to each other and are probably isomeric. S. B. A. A.

Parapropylisopropylbenzene. By M. Fileti (*Gazzetta*, **21**,4—22). —Paterno and Spica (this Journal, 1877, i, 77; Abstr., 1878, 296) first prepared isopropylpropylbenzene by the action of zinc ethyl on cumyl chloride. It is, however, more readily obtained in quantity by gently warming a mixture of dry ether (50 grams), metallic sodium (9 grams), parabromocumene (25 grams), and propyl bromide (31 grams). The reaction is sluggish at first, but soon becomes violent, and must be moderated by cooling with ice-cold water if necessary; it is completed in a few hours. The mass is then heated on the water-bath for some time, allowed to cool, sodium (3 grams) and propyl bromide (8 grams) added, the whole heated in a reflux apparatus for a couple of hours and fractionated. The yield is 59 per cent. The purified product boils at 213·5 to 215·5 (mercury column in the vapour) at a pressure of 745 mm. On oxidising parapropylisopropylbenzene with dilute nitric acid, the products consist of parapropylbenzoic acid crystallising in white, flattened needles melting at 139·5—140°, and impure terephthalic acid yielding on purification the characteristic methyl ether melting at 139—140°; but homoterephthalic acid does not appear to be formed, as stated by Paterno and Spica.

Mononitropropylisopropylbenzene, $C_{12}H_{17}NO_2$.—A yellow, oily compound of the above composition, rather heavier than water and decomposed on distillation, is obtained by treating the hydrocarbon with nitric acid (sp. gr. = 1·48), the whole being well cooled. The product is, however, a mixture of two isomeric compounds, as on reduction with ammonium sulphide, two *amido-derivatives* are obtained; one of these boils at 260—265°, and yields an acetyl derivative crystallising in slender needles and melting at 70—71°; the other is formed in less quantity, boils between 240° and 260°, and yields an acetyl derivative which crystallises in micaceous plates and melts at 87—88°. The *dinitro-derivative*, $C_{12}H_{16}(NO_2)_2$, is a yellow, oily compound heavier than water, and decomposes on distillation. The *monobromo-derivative*, $C_{12}H_{17}Br$, is a heavy, colourless liquid which boils at 265° (mercury column in the vapour) at a pressure of 738·6 mm. It probably has the constitution $C_6H_3BrPr^{\alpha}Pr^{\beta}$ [$Br : Pr^{\alpha} : Pr^{\beta} = 1 : 2 : 5$], since one of its products of oxidation is metabromocumic acid. On oxidising the bromo-derivative with dilute nitric acid, the products consist of ortho- and meta-parapropylbenzoic acids. On prolonging the oxidation for 25 hours, these acids are partially converted into metabromocumic acid.

Orthobromoparapropylbenzoic acid, $C_6H_3BrPr{\cdot}COOH$, crystallises when pure from light petroleum in long needles melting at 130—130·5°; on reduction with sodium, it yields parapropylbenzoic acid. The *metabromo-acid* crystallises from dilute alcohol in minute rhomboidal plates, but separates in an oily form from concentrated solutions. It melts at 108—109° and dissolves in all ordinary solvents except water. On reduction with sodium amalgam, parapropylbenzoic acid is formed together with a small quantity of a product melting at 291—292°.

Dibromopropylisopropylbenzene, $C_{12}H_{16}Br_2$, obtained by brominating the hydrocarbon in presence of iodine, is a heavy, colourless liquid which decomposes on distillation, and does not solidify in a mixture of ice and salt. *Dinitrodibromopropylisopropylbenzene*, $C_{12}H_{14}Br_2(NO_2)_2$, crystallises from light petroleum in tufts of slender, colourless or yellowish needles, melts at 124—125°, and dissolves freely in benzene, chloroform, carbon bisulphide, ether, and alcohol.

α-Propylisopropylbenzenesulphonic Acid.—On sulphonating propylisopropylbenzene, a mixture of the α- and β-sulphonic acids is obtained and is separated into its constituents by fractionally dissolving the mixed magnesium salts in boiling water. The α-acid is a white, crystalline, deliquescent compound which melts at 74° and dissolves in alcohol, ether, and benzene. The *sodium salt*, $C_{12}H_{17}SO_3Na,4H_2O$, crystallises in large plates very soluble in water; the *lead salt*, $(C_{12}H_{17}SO_3)_2Pb,H_2O$, crystallises from boiling water in tufts of needles or in nodules; the *barium salt*, $(C_{12}H_{17}SO_3)_2Ba,H_2O$, forms thin needles; the *magnesium salt*, $(C_{12}H_{17}SO_3)_2Mg,7H_2O$, crystallises from an aqueous solution in long, nacreous plates or tabular prisms, dissolves readily in boiling water but only very sparingly in the cold; the *zinc salt*, $(C_{12}H_{17}SO_3)_2Zn,8H_2O$, crystallises in elongated plates. The *acid chloride*, obtained by the action of phosphoric chloride on the dry sodium salt, is a yellowish liquid. The *amide*, $C_{12}H_{17}\cdot SO_2NH_2$, obtained by the action of gaseous ammonia on an ethereal solution of the chloride, crystallises from light petroleum in needles, melts at first at 93—94°, but after melting and resolidifying, the melting point falls to 79—80°. It dissolves readily in alcohol, ether, chloroform, and benzene, but is insoluble in cold water. The *anilide*, $C_{12}H_{17}\cdot SO_2\cdot NHPh$, forms nodular masses, melts at 107—109°, and dissolves in alcohol, chloroform, carbon bisulphide, and benzene, but not in water.

β-Propylisopropylbenzenesulphonic Acid. — The *magnesium salt*, $(C_{12}H_{17}SO_3)_2Mg,6H_2O$, forms crystalline tufts and is readily soluble in cold water. The *amide* crystallises from carbon bisulphide in nacreous plates, melts at 100—101°, and is freely soluble in alcohol, ether, &c., but is insoluble in cold water. S. B. A. A.

Reactions of Sodium Alkyloxides and Phenoxides with Tribromodinitrobenzene and Tribromotrinitrobenzene. By C. L. JACKSON and W. H. WARREN (*Amer. Chem. J.*, **13**, 164—193; compare Abstr., 1889, 781; 1890, 377, 497, 772, 982, 983).—These reactions take place in four different ways:—(1.) A simple replacement of each atom of bromine by the radicle of the alkyloxide or phenoxide. (2.) The replacement of two atoms of bromine by two of the radicle of the alkyloxide or phenoxide, the third atom of bromine remaining unaltered. (3.) The replacement of two atoms of bromine by the radicle and the third by hydrogen. (4.) The replacement of one, two, or, perhaps, three of the nitro-groups by the radicle, the three bromine atoms remaining unaffected.

The authors regard their data as affording insufficient ground for theoretical explanation; they point out that in case (4) the reaction is contrary to Laubenheimer's rule that a nitro-group is removed only when it is in the ortho-position to another nitro-group (*Ber.*, **9**, 766, 1828; this Journal, 1876, ii, 294; 1877, i, 594).

Diethylbromodinitroresorcinol, $C_6HBr(OEt)_2(NO_2)_2$, is the product of the action of sodium ethoxide on tribromodinitrobenzene (m. p. 192°) in the cold; full details of its preparation are given. It crystallises from alcohol in rather thick, flattened, yellowish-white needles, and from benzene in long, slender, efflorescent prisms; it melts at 184°, and is slightly soluble in alcohol, methyl alcohol, hot water, ether, and glacial acetic acid, freely soluble in acetone, less freely in benzene and chloroform, nearly insoluble in carbon bisulphide, and quite so in light petroleum. Hot and cold acids are without action on it. During its preparation a semi-liquid bye-product was obtained, but this proved of uncertain composition.

Diethyldinitroresorcinol, $C_6H_2(OEt)_2(NO_2)_2$, isomeric with Aronheim's compound (m. p. 75°, Abstr., 1879, 465) is formed when sodium ethoxide, dissolved in benzene, is heated with tribromodinitrobenzene (m. p. 192°) in alcohol. It crystallises in long, slender needles or flattened prisms with a sharp point, in some cases forming characteristic curling, hair-like crystals; it melts at 133°, dissolves best in chloroform, glacial acetic acid, and acetone, and forms a yellow solution in cold, strong sulphuric acid, but a colourless one in hot, strong nitric acid; hydrochloric acid has no action on it. It is noteworthy that this reaction is another example of the replacement of bromine by hydrogen in preference to its replacement by a radicle combined with sodium (compare Abstr., 1890, 497).

Diethylbromodinitroresorcinol may be converted into diethyldinitroresorcinol by heating it with sodium ethoxide in alcohol at the boiling point, showing that the replacement of the third bromine atom by hydrogen is the principal action of the hot sodium ethoxide.

Dimethylbromodinitroresorcinol was obtained, although not quite pure, when a solution of tribromodinitrobenzene in benzene was heated with a solution of sodium methoxide in methyl alcohol; it crystallises in prisms which, when deposited by cooling from glacial acetic acid, are terminated by a single rhombic plane at an acute angle to the sides of the prism, which are so short that the crystal looks like a rhombohedron; it melts at 237—238°, and is only slightly soluble in the common solvents. The *anilide*,

$$NHPh\cdot C_6H(OMe)_2(NO_2)_2,$$

forms bright yellow needles or very slender prisms, melts at 196°, and dissolves best in alcohol.

Dimethyldinitroresorcinol, $C_6H_2(OMe)_2(NO_2)_2$, is formed together with the bromo-derivative in the last-mentioned reaction whether the mixture is hot or cold. It crystallises (with 1 mol. alcohol) in bunches of white needles or slender prisms, which turn purplish-brown in air; also without alcohol in short, thick, broad, monoclinic (?), lemon-yellow prisms which are not altered by air; the former crystals are converted into the latter by recrystallisation from chloroform. It melts at 167°, but at 165·5° when it contains alcohol. It dissolves best in boiling alcohol; strong acids have little action on it. It is isomeric with Hönig's compound, which melts at 67° (Abstr., 1878, 727).

Diphenylbromodinitroresorcinol, $C_6HBr(OPh)_2(NO_2)_2$, is obtained, together with an oily substance and a small quantity of another crystalline substance (m. p. 158°), when tribromodinitrobenzene (1 mol.), dissolved in a mixture of benzene and alcohol, is heated with sodium phenoxide (3 mols.) in a reflux apparatus for 12 hours; it forms woolly masses of irregularly radiating, white needles which turn pale-brown in air; it melts at 165°, and dissolves best in a mixture of alcohol and benzene; it is apparently not acted on by strong sulphuric acid or hydrochloric acid, but is dissolved by strong nitric acid and precipitated by dilution as a new nitro- (?) derivative melting above 200°. Attempts to replace the bromine atom by hydrogen, as was done with the alkyl derivatives, proved futile.

Diethyltribromonitroresorcinol, $NO_2{\cdot}C_6Br_3(OEt)_2$, is obtained by the action of sodium ethoxide on tribromotrinitrobenzene (m. p. 285°) in alcohol, care being taken to avoid a rise of temperature; it crystallises in well-developed, white, flat prisms, usually with square ends, but sometimes terminated by two planes at an obtuse angle; it melts at 101°, and dissolves best in hot alcohol; the strong acids seem to have no action on it.

Tribromodinitrophenetoïl, $C_6Br_3(NO_2)_2{\cdot}OEt$, is formed if benzene as well as alcohol is used, and no care is taken to keep down the temperature, in the last-mentioned reaction. This crystallises in white, well-formed, slender, nearly square prisms, melts at 147°, dissolves best in hot alcohol, and is not acted on by strong acids.

Dimethyltribromonitroresorcinol, $C_6Br_3NO_2(OMe)_2$, obtained in the same manner as the diethyl compound, forms white, flattened prisms, melts at 126°, and is much less soluble in alcohol than the corresponding ethyl compound. Strong acids apparently have no action on it.

Triphenyltrinitrophloroglucinol, $C_6(NO_2)_3(OPh)_3$, is the product of the reaction of sodium phenoxide on tribromotrinitrobenzene in a mixture of alcohol and benzene at the temperature of the water-bath. It crystallises in long, very slender, white needles, felted together in woolly masses; it becomes brown in air, melts at 175°, and dissolves easily in acetone, chloroform, benzene, and glacial acetic acid, but slightly in other solvents. The strong acids have no apparent action on it. It is to be noted that the phenoxyl group is the most acid one which has been substituted for the three bromine atoms, the other groups which have been so substituted having been basic in character (compare Abstr., 1888, 1276; 1890, 247).

Neither sodium acetate, sodium picrate, nor sodium nitromethane has any but a slight action on tribromodinitrobenzene or tribromotrinitrobenzene.

It was previously shown (Abstr., 1890, 377, 485) that in the reaction between ethyl sodiomalonate and tribromodinitrobenzene the bromine atom replaced by hydrogen is between two nitro-groups, and experiments were made (Abstr., 1890, 983) which seemed to show that the ease with which the bromine is removed does not depend only on this position. These experiments have now been confirmed, and it is conclusively proved that ethyl malonate has no action on tribromodinitrobenzene. A. G. B.

Chloranil. By C. GRAEBE (*Annalen*, **263**, 16—31).—Chloranil (tetrachloroquinone) is best prepared by gradually adding potassium chlorate (250 grams) in coarse crystals to paraphenylenediamine hydrochloride (100 grams) suspended in water (250 c.c.) and hydrochloric acid (800 c.c.), or to the finely powdered base (60 grams) suspended in water (170—180 c.c.) and hydrochloric acid (920—950 c.c.). The addition of the chlorate lasts one day, and the temperature is maintained at 20—30°. On the following day, the mixture is slowly raised to the full temperature of the water-bath, and the heating is continued until all the chlorate is decomposed, when the crude chloranil is collected and washed. It appears to contain 25 per cent. of trichloroquinone, and when heated in a capillary tube filled with the substance and sealed at both ends, it usually melts at 220—240°; the yield is 115 grams. It is next heated on the water-bath for 1—2 hours with concentrated hydrochloric acid (350—400 c.c.), when a portion of the trichloroquinone is converted into tetrachloroquinol, and the remainder reacts with this, forming tetrachloroquinone and trichloroquinol. On oxidising the washed product with an acid solution of potassium dichromate, it is generally found to melt above 270°, and is then further purified by crystallisation from toluene. When quite pure, it melts at 290° (mercurial column entirely in the bath) to a clear, transparent liquid, whilst those specimens containing a slight quantity of impurity melt below this temperature, and darken considerably at their melting point.

Chloranilic acid is obtained when chloranil (10 grams) is moistened with alcohol and added to a solution of sodium hydroxide (9 grams) in water (200—220 c.c.) heated to 80°, or to a solution of potassium hydroxide (12 grams) in water (250 c.c.). After remaining 1—2 hours, common salt (20 grams) is added, and the precipitated sodium derivative is washed with a 10 per cent. solution of common salt until the filtrate is colourless; it is then redissolved in water, and the chloranilic acid precipitated with hydrochloric acid. The yield is 62 per cent. of the weight of the chloranil. The compound is conveniently prepared from the crude chloranil (m. p. above 270°); the moist product derived from 100 grams of paraphenylenediamine is treated with sodium hydroxide (100 grams) dissolved in water (2 litres); the yield is 46—50 grams. Chloranilic acid crystallises with 2 mols. H_2O, which it loses at 100°; 100 parts of water dissolve 0·19 part at 13·5°, and 1·41 parts at 99°; 1·77 parts of the potassium salt at 20°, and 9·25 parts at 98·6°; 1·06 parts of the sodium salt at 21°, and 6·19 parts at 99°.

When a mixture of trichloro- and tetrachloro-quinone is suspended in water (10 parts), and sulphurous anhydride is passed through for 10 minutes, the trichloro-derivative is converted into the quinol, and goes into solution, whilst the tetrachloro-derivative is scarcely attacked; the latter is collected and washed with water and cold alcohol. Tetrachloroquinol is formed when the quinone (10 grams) is heated for a short time on the water-bath with amorphous phosphorus (1 gram), water (15 c.c.), and 50 per cent. hydriodic acid (3—4 c.c.); it is filtered while hot, and the colourless mass dissolved in alcohol to free it from phosphorus. Hexachlorobenzene is obtained in accordance with the equation $C_6Cl_4O_2 + PCl_5 + PCl_3 = C_6Cl_6 + 2POCl_3$, when equal weights of chloranil, phosphorus pentachloride and trichloride are heated together in a sealed tube at 190—200° for four hours; as no gaseous products are formed, comparatively large quantities of material can be employed. When chloranil is heated with phosphorus pentachloride, with or without the addition of phosphorus oxychloride, hexachlorobenzene, a compound containing phosphorus, and probably the so-called hexachlorophenol are formed, and on treating the mixture with water, pentachlorophenol (m. p. 185—186°) may be separated. A. R. L.

Bromanil. By C. Graebe and L. Weltner (*Annalen*, **263**, 31—38).—Bromanil (tetrabromoquinone) is prepared by dissolving paraphenylenediamine (10 grams) in glacial acetic acid (40 c.c.), and carefully adding bromine (40 c.c.) by degrees to the solution kept cold by water. A solid mass soon forms, and it is advisable to shake from time to time; on the following day the product is heated on the water-bath until the evolution of hydrogen bromide and bromine slackens; water is then added, the heating continued for a short time, and the dark-brown substance collected, washed, and dried. It is then heated on the water-bath with nitric acid (sp. gr. 1·35, 40 c.c.) for some hours, and evaporated to dryness, after which it is again heated with fuming nitric acid (40 c.c.) for 2—3 hours, poured into water, and the yellow compound collected and washed; the yield is 30—32 grams, and the melting point of the product ranges from 280° to 285°. It is purified by crystallisation from toluene, and when quite pure melts at 300° (mercurial column entirely in the bath). When hexabromobenzene (2 grams) is heated with a mixture of nitric acid (sp. gr. 1·5, 25 c.c.) and sulphuric acid (15 c.c.) in a reflux apparatus for 15 hours, only a trace of bromanil is produced; whereas hexachlorobenzene, under similar conditions, yields half its weight of chloranil (compare Istrati, Abstr., 1890, 882).

Bromanilic acid is conveniently prepared from the crude moist bromanil. The product from 10 grams of paraphenylenediamine is dissolved in a solution of sodium hydroxide (20 grams) in water (450—500 c.c.), heated to 80°, and, after one or two hours, common salt (40—50 grams) is added, and the remainder of the operation conducted as with chloranilic acid (preceding abstract). When crystallised bromanil is used, 10 grams are moistened with alcohol and added to a solution of sodium hydroxide (6·2—6·5 grams) or potassium hydroxide (7·5 grams) in water (150 c.c.); the yield of bromanilic acid is 5·4 grams. The compound loses its water of crystallisation slowly at the ordinary temperature, but more quickly at 100°; 100 parts of water dissolve 0·145 part at 15·5°, and 2·25 parts at 99°; 5·06 parts of the potassium salt at 14°; 2·95 parts of the sodium salt at 21°.

When bromanil (1·5 grams) is heated at 190—200° for four hours with phosphorus pentachloride (3·8 grams) and phosphorus oxychloride (3—4 grams), hexachlorobenzene is obtained. It is quantitatively converted into hexabromobenzene when heated with four times its weight of a mixture of equal weights of phosphorus pentabromide and tribromide at 260—280° for four hours.

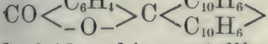
When dissolved in concentrated solutions of potassium sulphite, bromanil yields the potassium salt of thiocronic acid, whilst, when 1 gram is gently heated with a solution of potassium hydrogen sulphite (2·8 grams) in water (40 c.c.) until it dissolves, the potassium salt of *dibromoquinoldisulphonic acid*, $C_6Br_2(OH)_2(SO_3K)_2 + 2H_2O$, separates in colourless needles on concentrating the solution; it is easily soluble in hot water and in alcohol, and its solutions are coloured violet on addition of ferric chloride.

The *barium salt* is precipitated in colourless needles containing 1 mol. H_2O on adding barium chloride to a solution of the potassium salt; it is very slightly soluble in cold, but more so in hot, water.

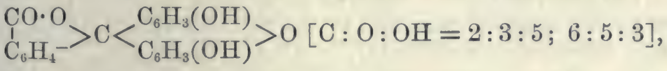
A. R. L.

Note by Abstractor.—The abstractor wishes to point out that he was the first to determine the melting point of bromanil (Trans., 1887, 148), but his value (288°) is too low, probably on account of the presence of a trace of impurity. He has redetermined the melting point of bromanil, and can confirm Graebe and Weltner's results, and also the melting point given by Graebe for chloranil (preceding abstract).

Phthaleïns. By R. Meyer (*Ber.*, **24**, 1412—1418).—β-Naphthol combines with phthalic chloride to form *naphtholphthaleïn anhydride*,



$CO{<}\substack{C_6H_4\\-O-}{>}C{<}\substack{C_{10}H_6\\C_{10}H_6}{>}O + \frac{1}{2}H_2O$; after treatment with acetic anhydride; this crystallises from alcohol in colourless, rhombic plates or needles, and melts at 115—117°. The compound dissolves in concentrated sulphuric acid, and the solution exhibits an intense reddish-yellow fluorescence. This is in accordance with the formula

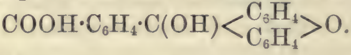


$$\begin{matrix}CO\cdot O\\ | \\ C_6H_4-\end{matrix}{>}C{<}\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}{>}O\ [C:O:OH = 2:3:5;\ 6:5:3],$$

previously advanced by the author for fluoresceïn.

Attempts to eliminate the amido-groups by the action of nitrous acid on the compound $C_{20}H_{15}N_3O_2$, which is formed by the interaction of ammonia and fluoresceïn at high temperatures, and has been already described, led to no definite result.

An investigation of residues obtained in the manufacture of phenolphthaleïn showed that they contained considerable quantities of phenolphthaleïn anhydride; this was deposited in crystals melting at 130—132°, they were, however, not homogeneous, and all the components have not yet been isolated.

Phenolphthaleïn anhydride melts at 180°, not at 173—175° as stated by Baeyer, and sublimes at much lower temperatures; it is readily soluble in alcoholic potash, and is not precipitated on dilution with water; after elimination of the alcohol, however, part is deposited immediately, and the remainder on addition of hydrochloric acid; this behaviour points to the formation of an unstable hydroxy-acid of the formula  $COOH\cdot C_6H_4\cdot C(OH)<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>O$. J. B. T.

Compounds of Metallic Sulphites with Aniline. By G. DENIGÈS (*Compt. rend.*, **112**, 802—805).—Normal metallic sulphites, with the exception of zinc sulphite, do not form compounds with aniline, but the hydrogen sulphites readily combine to form anhydrous double salts of the general formula $M''SO_3,H_2SO_3,2PhNH_2$. The mercuric salt is an exception, and has the composition

$$HgSO_3,H_2SO_3,PhNH_2 + H_2O.$$

They are obtained by adding sodium hydrogen sulphite to an acid solution of a sulphate or nitrate of the metal previously mixed with aniline; they form distinct hexagonal lamellæ, very slightly soluble in water and other neutral solvents. Aldehyde and acetone dissolve small quantities, but some chemical changes take place at the same time.

The cuprous compound is yellowish-white, and does not alter when exposed to air and light; it dissolves in ammonia and in hydrochloric acid. The cadmium and zinc compounds are white; the manganese salt has a pink tint, and the cobalt salt a beautiful rose colour; the ferrous salt is yellow, and the nickel salt greenish-yellow; the mercuric salt is white. C. H. B.

Some Compounds Formed by Mercuric Chloride. By G. ANDRÉ (*Compt. rend.*, **112**, 995—998).—A number of compounds are formed on the same type as the substance $HgCl_2,2NH_3$, described in a former paper (Abstr., 1889, 570 and 827). A white compound of aniline and mercuric chloride, $NH_2Ph,HgCl_2$, yields a little water on heating in a test-tube; hence it probably contains a little mercuric oxide, which would explain the excess of mercury obtained on analysis. A similar additive compound is obtained with benzylamine, $CH_2Ph\cdot NH_2,HgCl_2$. Similar substances, in which $HgCl_2$ is replaced by $ZnCl_2$, are represented by the formulæ $4ZnCl_2,HgCl_2,10NH_3 + 2H_2O$ and $2ZnCl_2,HgCl_2,6NH_3 + \frac{1}{2}H_2O$. These salts, when heated in a tube, give off water, melt, and finally yield a white sublimate together with free ammonia; they dissolve easily in hydrochloric acid, but are decomposed by boiling water.

Several new substitution compounds have also been prepared. The compound $5NHPh\cdot HgCl + 2HgCl_2$ is analogous to the substance $NH_2\cdot HgCl + HgCl_2$, obtained by Millon; it is very stable; when boiled with water or alcohol for several hours, it yields the salt $3NHPh\cdot HgCl + 2HgCl_2$.

The substitution compound, $CH_2Ph\cdot NH\cdot HgCl$, is insoluble in boiling water; the benzylamine addition compound is readily soluble. W. T.

Symmetrical Tri-substitution Derivatives of Benzene. By R. BADER (*Ber.*, **24**, 1653—1655).—*Symmetrical dinitraniline* is prepared by dissolving trinitrobenzene (15 grams) in absolute alcohol

(450 c.c.), and slowly adding to the boiling solution 90 c.c. of ammonium sulphide solution; after heating for $1\frac{1}{2}$ hours on the water-bath, the liquid is poured into ice-water; the product is deposited from hot water in yellow crystals, melts at 159°, and is readily soluble in ordinary media. Attempts to prepare the corresponding phenol by means of the diazo-reaction were unsuccessful.

Dinitrochlorobenzene [$NO_2 : NO_2 : Cl = 1 : 3 : 5$] is obtained from the preceding compound by means of Sandmeyer's reaction; it crystallises from alcohol or ether in colourless needles, melts at 53°, and is volatile with steam. On warming with very dilute alkalis, a blood-red colour is produced. J. B. T.

Combination of Metallic Sulphites with Amines of the Benzene Series. By G. DENIGÈS (*Compt. rend.*, **112**, 870—873).—Orthotoluidine, paratoluidine, and α-metaxylidine yield with metallic hydrogen-sulphites compounds strictly analogous to those formed by aniline (preceding page), they are obtained in the same manner, have the same colours and the same form. No compound of nickel hydrogen sulphite with orthotoluidine could, however, be obtained, and zinc hydrogen sulphite behaves in an abnormal manner. The general formula is $M''SO_3,H_2SO_3,2NH_2R$, but in the case of the mercuric compounds it is $HgSO_3,H_2SO_3,NH_2R + H_2O$.

C. H. B.

Nitro-derivatives of Dimethylorthanisidine. By E. GRIMAUX and L. LEFÈVRE (*Compt. rend.*, **112**, 727—730).—*Mononitrodimethylorthanisidine* [$NMe_2 : NO_2 : OMe = 1 : 4 : 6$] is obtained, together with a small quantity of a di- or tri-nitro-derivative, by adding 1 part of the base to 5 or 6 parts of nitric acid cooled in a freezing mixture, or, better, by dissolving 1 part of the base in 2 parts of sulphuric acid diluted with 10 parts of water, and adding gradually 3·2 parts of sodium nitrite dissolved in 60 parts of water. The product is purified by crystallisation from alcohol, and forms long, slender, lemon-yellow needles which melt at 99°; it is very slightly soluble in cold alcohol, but dissolves readily in boiling alcohol. When reduced with zinc and hydrochloric acid, it yields a base that crystallises in slender, colourless needles melting at 83°, and rapidly becomes rose-coloured when exposed to air.

Trinitrodimethylorthanisidine is obtained by heating dimethylorthoanisidine with ordinary nitric acid until nitrogen oxides begin to come off, and then precipitating immediately with water. It crystallises from boiling alcohol in groups of colourless, somewhat bulky prisms, melts at 135°, and is only slightly soluble in cold alcohol. Only two of the NO_2 groups are in the benzene nucleus, and when the compound is boiled with potash, alkaline vapours are evolved and dinitroguaiacol, melting at 121—122°, is obtained. This decomposition indicates the position of the radicles, namely

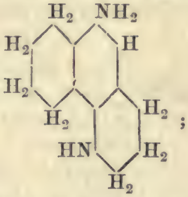
$$[NMe{\cdot}CH_2NO_2 : NO_2 : NO_2 : MeO = 1 : 2 : 4 : 6],$$

since von Romburgh has shown that only diortho-, or ortho- and para-derivatives of acids of the benzene series yield phenols when heated with potash.

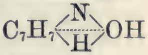
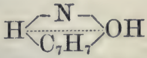
If trinitrodimethylorthanisidine is boiled with 15 to 20 parts of ordinary nitric acid until nitrogen oxides are no longer evolved, it is converted into *trinitromonomethylorthanisidine*, which is the ultimate product of the action of nitric acid on dimethylorthanisidine. It is also obtained by the prolonged action of fuming nitric acid on dimethylorthanisidine at 0°. It crystallises from 8 parts of boiling alcohol in colourless or yellowish lamellæ, melts at 118—119°, and is only slightly soluble in ether or in cold alcohol, but dissolves readily in acetone. When trinitromonomethylorthanisidine is heated for two or three hours with a 10 per cent. solution of potash, alkaline vapours are evolved, and the calculated quantity of dinitroguaiacol is obtained (m. p. 121—122°). This decomposition shows that the nitro-derivative has the constitution [$NMeNO_2 : NO_2 : NO_2 : OMe = 1 : 2 : 4 : 6$], and at the same time establishes the constitution of mononitrodimethylorthanisidine and dinitroguaiacol.

The results show that in the action of nitric acid on dimethylorthoanisidine, it is the group NMe_2 that influences the position of the NO_2 groups, the latter taking up ortho- and para-positions, as in the case of dimethylaniline. C. H. B.

1-4-6-Trimethylparaphenylenediamine. By E. BAMBERGER (*Ber.*, **24**, 1645—1649).—The author has recently obtained a paramidoctohydro-α-naphthaquinoline of the formula



the method of formation of this compound will be described later. Although a derivative of naphthaquinoline, its properties show it to be a benzeneparadiamine. For purposes of comparison, trimethylphenylenediamine [$Me_3 = 1 : 4 : 6$; $(NH_2)_2 = 2 : 5$] was prepared from pseudocumidine [$Me_3 = 1 : 4 : 6$; $NH_2 = 2$] by means of diazobenzenesulphonic acid; the resulting dye is deposited in reddish-brown, lustrous crystals, sparingly soluble in water. On reduction with stannous chloride, the diamine is obtained, crystallising from a mixture of ether and light petroleum in colourless, highly lustrous, flat needles melting at 78°. The diamine gives a dark, orange-red colour with hydrochloric acid, hydrogen sulphide, and ferric chloride (thionine); a deep-green, indamine colour with acetic acid, aniline hydrochloride, and potassium dichromate; on boiling, the solution changes to greenish-brown, then to reddish-brown, and smells of quinone. The base gives with metatolylenediamine the tolylene-blue and tolylene-red reactions; whilst with alkaline α-naphthol solution, a blue indophenol derivative is formed. J. B. T.

Alkyl Derivatives of Hydroxylamine. By R. BEHREND and E. KÖNIG (*Annalen*, **263**, 175—223 and 339—358).—At the present time there are three hypotheses regarding the structure of the stereochemically isomeric alkyl derivatives of hydroxylamine, namely, that of Hantzsch and Werner, that of Behrend, and that of Auwers and Meyer; they all account for the existence of two structurally identical but stereochemically isomeric forms, which bear to one another the same relationship as that existing between the two optically active modifications of tartaric acid. According to all three hypotheses, β-benzylhydroxylamine, for example, should exist in two enantiomorphous forms, which may be expressed by the symbols  $C_7H_7\left\langle\begin{matrix}N\\H\end{matrix}\right\rangle OH$ and  $H\left\langle\begin{matrix}-N-\\C_7H_7\end{matrix}\right\rangle OH$ respectively. Now, although this compound has been prepared by three totally different methods, the three preparations are absolutely identical; it must be assumed then, either that they all have the same configuration, expressed by one of the above symbols, or that they are all composed of equal parts of the two isomerides. If the latter assumption is true, it is probable that the two forms could be separated by suitable methods; the authors' attempts to effect a separation by combining the base with optically active acids were, however, unsuccessful, as were also the analogous experiments carried out by Kraft (this vol., p. 51). Experiments were also made to test the validity of the first assumption, namely, that the known β-benzylhydroxylamine is one only of the theoretically possible forms. For this purpose, β-benzylhydroxylamine was treated with nitrobenzyl chloride, and thus converted into β-benzylnitrobenzylhydroxylamine; β-nitrobenzylhydroxylamine, prepared by methods exactly similar to those employed in the preparation of the β-benzylhydroxylamine, was treated with benzyl chloride, and in this way also β-nitrobenzylbenzylhydroxylamine obtained. According to the hypothesis, the two compounds should be enantiomorphous, but it was found that they are identical in physical properties, and that both give the same products in the same proportion on oxidation; it follows, therefore, that assuming that no intramolecular change has occurred in any of the reactions, and that a second modification of benzylnitrobenzylhydroxylamine has not escaped observation, that the two supposed enantiomorphous forms of benzyl- and of benzylnitrobenzyl-hydroxylamine are identical, or, which is less probable, that their separation has not yet been accomplished.

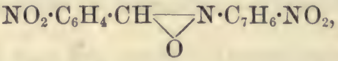
β-Benzylhydroxylamine tartrate, $(C_7H_9NO)_2,C_4H_6O_6$, is precipitated in needles when an alcoholic solution of the base (1 mol.) is treated with an alcoholic solution of tartaric acid (1 mol.); on evaporating the mother liquors, a second crop of crystals of the normal salt is obtained, and on further evaporation, the *acid tartrate*, $C_7H_9NO,C_4H_6O_6$, is deposited. The latter forms colourless, rhombic crystals, $a : b : c = 0{\cdot}3561 : 1 : 0{\cdot}2475$, is readily soluble in alcohol, and melts at about 117°; the former is sparingly soluble in alcohol, but more readily in water, and melts at 125—130°.

β-Benzylhydroxylamine mandelate crystallises from hot alcohol in colourless needles, melts at 115—118°, and is rather sparingly soluble in cold alcohol and water.

β-Diparanitrobenzylhydroxylamine, $(C_7H_6NO_2)_2N{\cdot}OH$, is obtained

when hydroxylamine hydrochloride is boiled with paranitrobenzyl chloride and sodium carbonate in alcoholic solution; it separates from boiling acetone in large, yellow, asymmetric crystals, melts at 157—158°, and is readily soluble in hot alcohol, glacial acetic acid, and acetone, but very sparingly in cold alcohol, ether, benzene, and chloroform, and almost insoluble in light petroleum and carbon bisulphide. The *hydrochloride*, $C_{14}H_{13}N_3O_5,HCl$, is crystalline, and is decomposed by water.

Paranitrobenzylisoparanitrobenzaldoxime,



$$NO_2\cdot C_6H_4\cdot CH\underset{O}{\diagdown\!\!\diagup}N\cdot C_7H_6\cdot NO_2,$$

prepared by oxidising the preceding compound with potassium dichromate and acetic acid, crystallises in light-yellow, microscopic needles, and is sparingly soluble or insoluble in most ordinary solvents, except hot acetic acid and boiling nitrobenzene; it melts at 227—228° with decomposition, but even when kept at 200° for some time, it gradually sinters together and turns brown. When boiled with 20 per cent. hydrochloric acid, it is decomposed into paranitrobenzaldehyde and β-nitrobenzylhydroxylamine (m. p. 120—125°), identical with the compound obtained by Behrend and Leuchs from α-benzyl-β-nitrobenzylhydroxylamine in like manner.

β-Paranitrobenzylbenzylhydroxylamine, prepared by treating the β-paranitrobenzylhydroxylamine obtained by the decomposition of α-benzyl-β-nitrobenzylhydroxylamine with benzyl chloride, is identical in chemical and physical properties with the compound formed by treating the β-nitrobenzylhydroxylamine, obtained from paranitrobenzylisoparanitrobenzaldoxime with benzyl chloride, and also with that produced by the action of nitrobenzyl chloride on β-benzylhydroxylamine.

Nitrobenzylisobenzaldoxime exists in two modifications, both of which are formed when benzaldehyde is digested with β-nitrobenzylhydroxylamine hydrochloride and sodium carbonate in alcoholic solution; the original product melts at 104—106°, but when recrystallised from hot alcohol it yields a mixture of slender needles melting at 113·5—114·5°, and hexagonal plates melting at 105—106°. These two forms can be easily converted one into the other by recrystallisation from various solvents, and when either modification is heated at its melting point it is converted into a mixture of the two which melts at 107—112°. When equal quantities of nitrobenzylisobenzaldoxime and benzilisonitrobenzaldoxime are dissolved in hot alcohol and the solution concentrated, a mixture of the two compounds is deposited in plates melting at 93—94°; this mixture is identical with that obtained by the oxidation of paranitrobenzylbenzylhydroxylamine (Abstr., 1890, 1412).

Nitroso-β-benzylhydroxylamine, $C_7H_8N_2O_2$, is obtained when β-benzylhydroxylamine hydrochloride is treated with sodium nitrite in aqueous solution at 0°; it crystallises from a mixture of ether and light petroleum in flat, transparent prisms, melts at 77—78°, and is readily soluble in alcohol, ether, soda, and sodium carbonate, but more sparingly in light petroleum and very sparingly in water; it gives the nitroso-reaction. The *benzyl* derivative, $C_{14}H_{14}N_2O_2$, is formed, together with an oil of unknown composition, when the sodium derivative of nitrosobenzylhydroxylamine is boiled with benzyl chloride in alcoholic solution; it crystallises from a mixture of ether and light petroleum in lustrous plates, melts at 58—59°, and gives Liebermann's reaction. When α-dibenzylhydroxylamine hydrochloride is treated with sodium nitrite, it is converted into a compound which crystallises in needles and melts at 73—74°.

Impure nitroso-β-benzylhydroxylamine is unstable, and decomposes on keeping with liberation of red fumes, yielding dinitrosylbenzyl (previously described as dinitrosotoluene, Abstr., 1890, 1122) and an oil having a peculiar, penetrating odour; when treated with glacial acetic acid, the nitroso-compound is decomposed into dinitrosylbenzyl and an oil, which consists principally of benzyl acetate and benzyl nitrite.

Nitroso-β-paranitrobenzylhydroxylamine, $NO_2{\cdot}C_7H_6{\cdot}N(NO){\cdot}OH$, is precipitated in crystals when a freshly-prepared, well-cooled solution of β-paranitrobenzylhydroxylamine hydrochloride is treated with a slight excess of the theoretical quantity of sodium nitrite; it sinters together at 125°, melts at 130—131°, and is readily soluble in alcohol, acetone, sodium carbonate, and glacial acetic acid, but more sparingly in chloroform and ether; it gives Liebermann's reaction. When dissolved in glacial acetic acid and treated with a trace of fuming nitric acid, it is decomposed, with evolution of brown fumes, yielding dinitrosylparanitrobenzyl, paranitrobenzyl acetate (m. p. 76—77°), and a compound melting at about 67°, which seems to be paranitrobenzyl nitrite.

Dinitrosylparanitrobenzyl, $C_{14}H_{12}N_4O_6$, is a colourless, semi-crystalline powder, melts at 135—140°, and is almost insoluble in the ordinary solvents; when treated with phenol and sulphuric acid, it gives a brownish-violet coloration, which changes to brownish-yellow on the addition of alkalis, and then to an olive-brown on diluting with water.

β-Paranitrobenzaldoxime, $C_7H_6N_2O_3$, is obtained, together with an equal quantity of the α-compound (m. p. 128—129°) when dinitrosylparanitrobenzyl is warmed with dilute soda (or boiled for a long time with alcohol); on saturating the alkaline solution with carbonic anhydride, the two isomerides are precipitated in crystals, and can be separated by recrystallisation from hot water, in which the β-compound is the more sparingly soluble. The β-oxime crystallises from hot water in thin, iridescent, rectangular plates, sinters together at about 170°, melts at 173—175°, and is readily soluble in glacial acetic acid, chloroform, and hot alcohol, but more sparingly in ether; when heated at its melting point, or when treated with hydrogen chloride in ethereal solution, it is almost completely converted into the α-oxime, and it is readily decomposed by warm mineral acids yielding nitrobenzaldehyde and hydroxylamine. When the acetyl derivative of the β-oxime is treated with sodium carbonate, it is converted into paranitrobenzonitrile, whereas the acetyl derivative of the α-oxime is simply reconverted into the oxime (m. p. 128—129°) under the same conditions.

Benzylparanitrobenzaldoxime, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OC_7H_7$, is formed when the α-oxime is treated with sodium ethoxide and benzyl chloride in cold alcoholic solution; it crystallises from alcohol in lustrous, yellowish needles, melts at 117·5—118·5°, and differs slightly in crystalline form from the isomeride (m. p. 117—118°) previously described (Abstr., 1890, 1412), than which it is rather more sparingly soluble in hot alcohol; it is not acted on by boiling dilute acids, whereas the isomeride is quickly decomposed into nitrobenzaldehyde and β-benzylhydroxylamine.

When β-paranitrobenzaldoxime is treated with sodium chloride and benzyl chloride in alcoholic solution at the ordinary temperature, it yields benzylisoparanitrobenzaldoxime and paranitrobenzylisobenzaldoxime.

Dinitrosobenzyl (*loc. cit.*) is completely decomposed by warm soda, yielding approximately equal quantities of α- and β-benzaldoxime.

F. S. K.

Azo-derivatives. By H. Limpricht (*Annalen*, **263**, 224—245).—Azobenzenesalicylic acid, $N_2Ph\cdot C_6H_3(OH)\cdot COOH$, prepared by treating salicylic acid with diazobenzene chloride in alkaline solution (compare Stebbins, Abstr., 1880, 715), crystallises from benzene in yellow needles, melts at 218°, decomposes at a slightly higher temperature, and is readily soluble in alcohol, ether, and acetone, but more sparingly in boiling chloroform and carbon bisulphide, and almost insoluble in water. The *sodium* salt, $C_{13}H_9N_2O_3Na$, crystallises in small, yellow plates; the *barium* salt, $(C_{13}H_9N_2O_3)_2Ba$, crystallises in golden needles, and is very sparingly soluble in cold water. The acid is quickly decomposed by stannous chloride into aniline and paramidosalicylic acid; the last-named compound is also formed when the azo-acid is warmed with zinc-dust and soda. The ethereal salts of azobenzenesalicylic acid can be obtained by warming the acid with an alcohol and concentrated sulphuric acid; by dissolving the acid in the alcohol, and heating the solution at 100° with the corresponding alkyl iodide, and also by treating ethereal salts of salicylic acid with diazobenzene chloride in alkaline solution. The *methyl* salt,

$$C_{14}H_{12}N_2O_3,$$

crystallises in reddish-yellow plates, melts at 108°, and is readily soluble in alcohol, ether, and soda. The *ethyl* salt, $C_{15}H_{14}N_2O_3$, crystallises in yellowish needles or plates, melts at 101°, and is readily soluble in alcohol, ether, and dilute soda; it distils at a high temperature with only slight decomposition, and is decomposed by stannous chloride yielding ethyl amidosalicylate. The *phenyl* salt, $C_{19}H_{14}N_2O_3$, is formed, together with phenyl bi-azobenzenesalicylate, when an ice-cold alkaline solution of phenylsalicylate is treated with diazobenzene chloride; it separates from ether in yellowish-red needles, and from cold alcohol in well-defined crystals, melts at 121°, and is readily soluble in ether, chloroform, and benzene, but more sparingly in alcohol, acetone, carbon bisulphide, glacial acetic acid, and soda.

Phenyl bi-azobenzenesalicylate, $OH\cdot C_6H_2(N_2Ph)_2\cdot COOPh$, forms compact, granular crystals, melts at 148°, and is readily soluble in alcohol, ether, chloroform, benzene, acetone, glacial acetic acid, and soda.

Azobenzenesalicylamide, prepared by heating the methyl or ethyl salt of the acid with ammonia, crystallises in light-yellow needles, and melts at 240°, not at 236°, as stated by Tummely. The *anilide*, $OH{\cdot}C_6H_3(N_2Ph){\cdot}CO{\cdot}NHPh$, can be obtained by treating salicylamide with diazobenzene chloride in alkaline solution; it crystallises from alcohol in brown plates, melts at 188—189°, and is readily soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid; it dissolves in concentrated sulphuric acid with a blood-red coloration.

Azobenzenechlorobenzamide, $N_2Ph{\cdot}C_6H_3Cl{\cdot}CO{\cdot}NH_2$, is formed when azobenzenesalicylic acid is heated with phosphorus pentachloride, and the product treated with ammonia; it separates from alcohol in yellow crystals melting at 210°. The corresponding *anilide*,

$$N_2Ph{\cdot}C_6H_3Cl{\cdot}CO{\cdot}NHPh,$$

prepared in like manner, separates from alcohol in yellowish, nodular crystals, and melts at 198°.

Azobenzenemetahydroxybenzoic acid, $OH{\cdot}C_6H_3(N_2Ph){\cdot}COOH$, separates from benzene in golden crystals, melts at 213°, and is readily soluble in alcohol, ether, chloroform, acetone, glacial acetic acid, and soda, but only sparingly in benzene; when warmed with stannous chloride, it yields *metahydroxyamidobenzoic acid* [$OH : COOH : NH_2 = 1 : 3 : 4$], a colourless, crystalline compound, which darkens at 230°, and melts at 235°; when this amido-acid is diazotised, and the product warmed with hydriodic acid, *iodometahydroxybenzoic acid* is obtained. This compound crystallises from water in large, yellowish needles, sublimes at 160—170°, melts at 196°, and seems to have the composition $C_7H_5IO_3 + \frac{1}{2}H_2O$; when treated with sodium amalgam, it is converted into metahydroxybenzoic acid.

When parahydroxybenzoic acid is treated with diazobenzene chloride in ice-cold, alkaline solution, bi-azobenzenephenol (m. p. 130°), and azobenzenephenol (m. p. 150—151°) are formed, but no azo-derivative of hydroxybenzoic acid is produced. The compound, obtained by treating parahydroxybenzoic acid with diazosulphanilic acid in ice-cold alkaline solution, has not the constitution

$$SO_3H{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_3(OH){\cdot}COOH,$$

as supposed by Griess (*Ber.*, **15**, 2190), but is the sodium salt of a hydroxyparazobenzenesulphonic acid of the constitution

$$OH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H.$$

This acid is identical with the compound formed by the combination of phenol and diazosulphanilic acid; its *sodium* salt crystallises in reddish-yellow, lustrous scales, is readily soluble in hot water, and has the composition $OH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3Na + 2H_2O$; its *barium* salt crystallises from hot water in red, lustrous, rhombic plates ($+ H_2O$), and in yellow needles ($+ 1\frac{1}{2}H_2O$), and is very sparingly soluble in cold water.

Azo-derivatives of paramethoxybenzoic acid could not be obtained.

Azobenzene-β-resorcylic acid, $N_2Ph{\cdot}C_6H_2(OH)_2{\cdot}COOH$, is formed, together with bi-azobenzeneresorcinol (m. p. 217°) when β-resorcylic acid is treated with diazobenzenzene chloride in ice-cold, alkaline solution; it crystallises from acetone in dark-red needles, melts at about 189° with evolution of carbonic anhydride, and is readily soluble in chloroform and hot alcohol, but more sparingly in ether, benzene, and acetone, and insoluble in water; it is partially decomposed by recrystallisation from acetone, yielding bi-azobenzeneresorcinol, with evolution of carbonic anhydride. F. S. K.

Orthohydroxyazo-dyes. By S. v. KOSTANECKI and J. D. ZIBELL (*Ber.*, **24**, 1695—1699).—The authors have studied the azo-dyes from the hydroxybenzoic acids, and find that the action of diazobenzene chloride on parahydroxybenzoic acid is quite different to its action on the ortho- and meta-acids.

Phenylazosalicylic acid and phenylazometahydroxybenzoic acid are best obtained by adding diazobenzene chloride to the hydroxybenzoic acid in the presence of sodium carbonate. The dye is precipitated from the soda solution with acid, and crystallised from alcohol. Phenylazosalicylic acid decomposes at 211°; phenylazohydroxybenzoic acid at 205°. The latter does not dye mordanted cotton.

Parahydroxybenzoic acid and diazobenzene chloride yield a product which is only partly soluble in sodium carbonate. The soluble portion crystallises from dilute alcohol, in which it is easily soluble, in orange tablets, melts at 150°, and was identified as phenylazophenol. The insoluble portion crystallises from alcohol in brownish-red leaflets, melts at 131°, and was identified as phenyldisazophenol. Thus parahydroxybenzoic acid reacts with diazobenzene chloride in the same way as β-naphtholcarboxylic acid (m. p. 157°), which also loses the carboxyl group.

Griess (Abstr., 1883, 182; 1884, 1013) has stated that parahydroxybenzoic acid reacts with diazosulphanilic acid in the same way as salicylic and metahydroxybenzoic acids. The authors, however, find that when diazosulphanilic acid is added to a solution of parahydroxybenzoic acid containing sodium carbonate, a compound is obtained crystallising in golden-yellow leaflets, which answers to the description of the compound obtained by Griess, and gives on analysis numbers agreeing with his numbers. These numbers, however, agree with the formula $SO_3Na\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot OH + 2H_2O$. The authors have made a complete analysis of the compound, and find that it is identical with the sodium salt of the compound obtained from diazosulphanilic acid and phenol.

The authors were unable to obtain azo-dyes of parahydroxybenzoic acid by the action of diazobenzene chloride or diazosulphanilic acid on parahydroxybenzoic acid, under many varying conditions.

E. C. R.

Tetrazotic Acids, Oxy- and Dioxytetrazotic Acids. By W. LOSSEN (*Annalen*, **263**, 73—80).—The author and Mierau have previously shown that an acid of the composition $C_7H_6N_4O_2$ can be obtained by treating benzenylamidine nitrite with mineral acids; the further investigation of this subject has brought to light the following facts.

Other amidines containing the atomic complex $NH{:}C\cdot NH_2$ give acids analogous in composition to that produced from benzenylamidine, but those amidines in which the hydrogen of the amido- or imido-group has been substituted by an alkyl group give no such compounds.

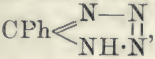
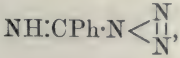
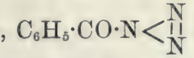
The acids prepared from the amidines have the general formula $X{\cdot}CN_4O_2H$; on treatment with sodium amalgam, they lose either one or two atoms of oxygen, yielding acids having the composition $X{\cdot}CN_4OH$ and $X{\cdot}CN_4H$ respectively.

The oxygen-free compound obtained from benzenylamidine has the molecular formula $C_7H_6N_4$, and is a strong monobasic acid. Judging from its decomposition products, it contains the unchanged benzenyl group, and may, therefore, be named benzenyltetrazotic acid; the compound of the composition $C_7H_6N_4O$ may be termed benzenyloxytetrazotic acid, and the compound of the composition $C_7H_6N_4O_2$ benzenyldioxytetrazotic acid.

The dioxytetrazotic acids are very unstable in the free state, and have not yet been isolated; their salts are much more stable in solution, but all the metallic salts are highly explosive in the dry state, and must be handled with the greatest care; they are also decomposed by concentrated sulphuric acid with explosive violence.

The only oxytetrazotic acid yet prepared is benzenyloxytetrazotic acid; as regards stability, it seems to be intermediate between benzenyltetrazotic acid and benzenyldioxytetrazotic acid; the anhydrous compound readily decomposes, but when in combination with 1 mol. of water of crystallisation it is stable.

The tetrazotic acids are very stable; benzenyltetrazotic acid is decomposed by concentrated hydrochloric acid and by potash only at a high temperature.

The constitution of these new compounds has not yet been determined, and there are but few facts from which any conclusions can be drawn. It is probable, in the first place, that since benzenyldioxytetrazotic acid gives benzonitrile on decomposition, it contains the group $CPh{\equiv}$, and since it is formed by the action of nitrous acid on the amidine, its constitution is probably represented by the formula $NO{\cdot}N{:}CPh{\cdot}N{:}N{\cdot}OH$; this view is in accordance with the fact that substituted amidines give no analogous compound, and also with the reactions of the acid and with those of its derivatives. Benzenyltetrazotic acid is probably also a benzenyl derivative, as it is formed by the action of sodium amalgam on a cold dilute solution of the dioxytetrazotic acid: when heated with concentrated hydrochloric acid, it is decomposed into aniline, carbonic anhydride, nitrogen, and ammonia, and its ethyl salt under the same conditions gives benzoic acid, ammonia, nitrogen, a little carbonic anhydride, and probably also aniline, ethylamine, and ethyl chloride; it may possibly be a tetrazole derivative of the constitution  $\mathrm{CPh}{<}\begin{array}{l}\mathrm{N{-}N}\\ \qquad\ \ \|\\ \mathrm{NH{\cdot}N}\end{array}$, or it may have the constitution  $\mathrm{NH{:}CPh{\cdot}N}{<}\begin{array}{l}\mathrm{N}\\ \|\\ \mathrm{N}\end{array}$, in which case it would be the imido-derivative of Curtius' benzoylazoimide,  $\mathrm{C_6H_5{\cdot}CO{\cdot}N}{<}\begin{array}{l}\mathrm{N}\\ \|\\ \mathrm{N}\end{array}$ (this vol., p. 56).

An account of the experimental work on this subject is given in the following abstracts. F. S. K.

Benzenyldioxytetrazotic Acid. By W. Lossen and F. Mierau (*Annalen*, **263**, 81—87).—*Benzenylamidine benzenyldioxytetrazotate*, $C_7H_8N_2,C_7H_6N_4O_2$, is best prepared by mixing an aqueous solution (80 c.c.) of potassium nitrate (80 grams) with a solution of benzenylamidine hydrochloride (20 grams) in water (100 grams) heated at 60—70°, and then adding, drop by drop, sulphuric acid of sp. gr. 1·2 (20 c.c.); after keeping for two hours, the precipitated salt is separated by filtration. The yield is, at the most, 37 grams from 100 grams of the hydrochloride; during the process nitric oxide and nitrogen are evolved, and some of the product undergoes decomposition with formation of benzonitrile. It crystallises from boiling alcohol in lustrous plates, explodes at about 178°, and is readily soluble in hot alcohol, but only sparingly in hot water, and almost insoluble in ether. The *potassium* salt, $C_7H_5N_4O_2K$, is deposited in crystals when the benzenylamidine salt is treated with alcoholic potash, or with an alcoholic solution of potassium acetate; it crystallises in needles or plates, explodes violently when heated, when rubbed, or when brought into contact with concentrated sulphuric acid, and is very readily soluble in water, but only sparingly in cold alcohol, and insoluble in ether. The *silver* salt, $C_7H_5N_4O_2Ag$, is obtained as a white precipitate on adding a solution of silver nitrate to a solution of the potassium salt; it is very explosive. In solutions of the potassium salt, barium chloride, lead acetate, and mercurous nitrate produce colourless precipitates, which are explosive in the dry state; solutions of ammonium chloride, hydroxylamine hydrochloride, and methylaniline hydrochloride give crystalline precipitates, and a solution of rosaniline gives a voluminous, dark-red precipitate.

The free *benzenyldioxytetrazotic* acid is very unstable; on adding a mineral acid to a solution of the potassium salt, the liquid turns yellow, but becomes colourless again on warming, nitrogen and nitric oxide being evolved, with formation of benzonitrile.

F. S. K.

Metanitrobenzenyldioxytetrazotic Acid. By W. Lossen and M. Neubert (*Annalen*, **263**, 87—92).—*Potassium metanitrobenzenyldioxytetrazotate*, $NO_2{\cdot}C_7H_4N_4O_2K$, is deposited in crystals, together with the corresponding amidine salt, when a solution of metanitrobenzenylamidine hydrochloride is mixed with excess of a concentrated solution of potassium nitrite, and nitric acid added to the mixture until a regular evolution of gas takes place; the two compounds can be separated by treating the mixture with hot water or hot alcohol, in both of which the amidine salt is almost insoluble. The potassium salt can also be obtained by boiling the amidine salt with a concentrated solution of potassium nitrite, or by agitating it with alcoholic potash. It crystallises from hot alcohol in small, moss-like needles, is very explosive, gives Liebermann's reaction, and is only sparingly soluble in cold water and cold alcohol. The free acid could not be isolated; when a solution of the potassium salt is treated with strong mineral acids, and when the lead salt is decomposed with hydrogen sulphide, metanitrobenzonitrile is formed with evolution of gas. The *barium* salt, $(NO_2{\cdot}C_7H_4N_4O_2)_2Ba$, prepared by precipitating a solution of the potassium salt with barium chloride, is a colourless, explosive compound almost insoluble in water and alcohol. The *silver* salt, $NO_2\cdot C_7H_4N_4O_2Ag$, is a dirty-white, explosive compound, very sensitive to light. The *ammonium* salt,

$$NO_2\cdot C_7H_4N_4O_2\cdot NH_4,$$

is precipitated in needles on adding ammonium chloride to a solution of the potassium salt; it is sparingly soluble in water, but readily in alcohol, and explodes at about 152°. The *hydroxylamine* salt, $NO_2\cdot C_7H_5N_4O_2,NH_2\cdot OH$, crystallises in needles, and is rather explosive. The *phenylhydrazine* salt, $NO_2\cdot C_7H_5N_4O_2,N_2H_3Ph + H_2O$, crystallises in yellowish needles, and melts at about 130° with decomposition; in solutions of the potassium salt, the hydrochlorides of aniline and metaphenylenediamine also produce crystalline precipitates. The *metanitrobenzenylamidine* salt, $NO_2\cdot C_7H_5N_4O_2,NO_2\cdot C_7H_7N_2$ (see above), is a yellow, crystalline powder which melts at about 176°, and is insoluble in the ordinary solvents; it is rapidly decomposed by concentrated sulphuric acid, but only slowly by dilute hydrochloric acid. The ethyl salt seems to be decomposed by alcohol. F. S. K.

Phenethenyldioxytetrazotic Acid. By W. and C. LOSSEN (*Annalen*, **263**, 92—95).—*Phenethenylamidine phenethenyldioxytetrazotate*, $C_7H_{10}N_2,C_8H_8N_4O_2$, is gradually precipitated when a solution of phenethenylamidine nitrite (10 grams) in water (150—200 c.c.) at about 60° is mixed with a saturated solution (10—15 c.c.) of potassium nitrite, and then dilute sulphuric acid added until the evolution of gas commences; the yield is, at the most, 20 grams from 100 grams of the amidine salt. It crystallises from hot alcohol in slender needles, and from water in well-defined, rhombic crystals, $a : b : c = 0·551 : 1 : 0·407$, is moderately easily soluble in alcohol, but only sparingly in ether, and almost insoluble in cold water; it is decomposed by boiling water with formation of phenylacetonitrile. The *potassium* salt, $C_8H_7N_4O_2K$, prepared by triturating the amidine salt with alcoholic potash, crystallises from boiling alcohol in large, nacreous plates, and is readily soluble in water, but only sparingly in cold alcohol, and insoluble in ether; its aqueous solution undergoes decomposition on boiling, with formation of phenylacetonitrile, and the dry compound is highly explosive. The *silver* salt, $C_8H_7N_4O_2Ag$, is obtained as a reddish precipitate on adding silver nitrate to a solution of the potassium salt; it first becomes colourless, but on exposure to light again turns reddish, then brown, and finally black; it is highly explosive, and is very readily decomposed by alkalis.

F. S. K.

Reduction of Benzenyldioxytetrazotic Acid. By W. and C. LOSSEN (*Annalen*, **263**, 96—108).—*Benzenyloxytetrazotic acid* and *benzenyltetrazotic acid* are both produced when an aqueous solution of the potassium salt of benzenyldioxytetrazotic acid is reduced with sodium amalgam; the two products cannot be easily separated. When a warm concentrated solution of the potassium salt of the dioxy-acid is treated with excess of sodium amalgam, benzenyloxytetrazotic acid is the sole product, whereas when a cold 6—8 per cent. solution of the potassium salt is employed, only a small quantity of benzenyloxytetrazotic acid is formed, the principal product being benzenyltetrazotic acid.

Benzenyloxytetrazotic acid, $C_7H_6N_4O + H_2O$, crystallises from boiling water in needles, and from cold dilute alcohol in reddish-yellow, rhombic or monosymmetric forms; it loses its water at 150°, melts at 175° with explosive decomposition, and is soluble in alcohol and ether, but is reprecipitated from the solutions on the addition of light petroleum. The anhydrous acid readily undergoes decomposition, on keeping, with evolution of nitrous fumes; it seems, also, to be decomposed by anhydrous solvents, such as benzene, even at the ordinary temperature, but it is not acted on by boiling hydrochloric acid or dilute sulphuric acid. Concentrated nitric acid decomposes it in the cold, but concentrated sulphuric acid has no action until the temperature rises to about 250°; the solution in hot sulphuric acid gives Liebermann's reaction, whereas the undecomposed acid does not. The results of molecular-weight determinations in phenol solution were in accordance with those required by a compound of the molecular formula given above. The *potassium* salt, $C_7H_5N_4OK$, separates from alcoholic ether in crystals, is readily soluble in water and alcohol, and explodes when heated. The *barium* salt, $(C_7H_5N_4O)_2Ba + 3H_2O$, crystallises in plates, loses its water at 105°, and is readily soluble in water, but more sparingly in alcohol. The *silver* salt, $C_7H_5N_4OAg$, is insoluble in water, and darkens on exposure to light. In solutions of the potassium salt, the nitrates of lead and mercury produce a colourless, copper sulphate a light-green, and ferric chloride a reddish-brown precipitate.

Benzenyltetrazotic acid, $C_7H_6N_4$, crystallises from hot water in long, colourless needles, and from cold alcohol in rhombic forms, melts at 212—213° with decomposition, and is moderately easily soluble in alcohol, but only sparingly in ether, and almost insoluble in benzene, light petroleum, and cold water. When the acid is carefully heated at its melting point, it turns wine-red, and, on cooling, the liquid solidifies to a colourless mass, in which is imbedded a small quantity of a purple-red substance, insoluble in water, and only sparingly soluble in dilute alcohol; when heated quickly, the acid decomposes suddenly, with development of light and heat, yielding a thick, dark-green, very stable liquid, which is readily soluble in alcohol. Molecular-weight determinations in phenol solution gave results in accordance with those required by the molecular formula $C_7H_6N_4$. The *potassium* salt, $C_7H_5N_4K$, crystallises from alcoholic ether in nacreous plates, and decomposes on heating. The *barium* salt, $(C_7H_5N_4)_2Ba + 3H_2O$, crystallises in thin plates. The *silver* salt, $C_7H_5N_4Ag$, is colourless, and moderately stable in the light. Copper sulphate, silver nitrate, and the two nitrates of mercury produce precipitates in an aqueous solution of the acid, and, with a solution of the potassium salt, mercuric chloride and lead nitrate give a colourless, cobalt nitrate a bright-red, and ferric chloride a yellowish-brown precipitate. The *ethyl* salt, $C_7H_5N_4Et$, prepared by heating the acid with an alcoholic solution of potassium ethoxide and ethyl iodide, is a moderately thick oil, insoluble in water, but soluble in alcohol, ether, and concentrated hydrochloric acid; it cannot be distilled.

F. S. K.

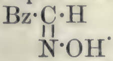
Orthochlorophenylhydrazine. By C. Willgerodt (*Ber.*, **24**, 1660—1662).—Orthochlorophenylhydrazine hydrochloride is obtained by reduction of orthochlorodiazobenzene chloride with stannous chloride and hydrochloric acid. It is a white, crystalline compound, and decomposes about 200°.

Orthochlorophenylhydrazine is obtained as a white, crystalline mass on adding excess of strong ammonia to an aqueous solution of the hydrochloride. It is soluble in hot water, alcohol, ether, and benzene, and is fairly stable to light, air, and a gentle heat.

Picrylorthochlorophenylhydrazine is obtained by mixing hot alcoholic solutions of the hydrazine hydrochloride and picryl chloride. It crystallises in thick, red prisms, and melts at 160°. From benzene, it crystallises in yellow plates containing 1 mol. of benzene, which it loses when heated at 100°. From pseudocumene, or from an alcoholic solution of pseudocumene, it crystallises in thick, yellow prisms containing 1 mol. of the hydrocarbon, which it loses when heated at 100°.

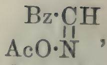
Dinitronitrosophenylorthochlorazobenzene, $C_6H_4Cl{\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO$, is obtained by boiling picrylorthochlorophenylhydrazine with acetic acid in a reflux apparatus. It crystallises in yellowish-red prisms, melts at 244—245°, and is quite insoluble in benzene.

E. C. R.

Configuration of ω-Isonitroacetophenone (Benzoylformoxime). By H. G. Söderbaum (*Ber.*, **24**, 1381—1388).—An acetyl derivative could not be obtained by the interaction of benzoylformoxime and acetic anhydride; benzoic cyanide was the only product; its formation, however, proves that the oxime belongs to the β-series, and has the formula  $\begin{array}{c}\mathrm{Bz{\cdot}C{\cdot}H}\\ \|\\ \mathrm{N{\cdot}OH}\end{array}$. On treating the oxime with acetic chloride at the ordinary temperature, a compound is deposited of the formula $C_{10}H_{10}NO_3Cl$; Claisen and Manasse, who first prepared it, supposed it to be the acetyl derivative; in all probability, however, it is either the *oximacetate hydrochloride*, BzCH:N·OAc,HCl, or a hydroxychloride of the same oximacetate, of the formula

OH·CPhCl·CH:NOAc.

By the action of water at the ordinary temperature, the hydrate of *benzoylformoxime acetate*, $CPh(OH)_2{\cdot}CH{:}NOAc$ is formed, crystallising from chloroform in colourless, lustrous needles which melt at 131°. The oxime is regenerated on warming with dilute hydrochloric acid or by treatment with concentrated sulphuric acid at the ordinary temperature. The acetyl derivative yields phenylhydroxyacetic acid on hydrolysis with dilute soda; with sodium carbonate solution, however, *diphenylhydroxytriketone*, OH·CHBz·COBz, is formed, and crystallises from benzene in yellow, microscopic needles melting at about 170°; the molecular weight, determined by Raoult's method, agrees with the formula.

The above oximacetate appears to be the α-modification  $\begin{array}{c}\mathrm{Bz\cdot CH}\\ \|\\ \mathrm{AcO\cdot N}\end{array}$, and is probably formed from the intermediate β-derivative by molecular rearrangement induced by the action of hydrogen chloride. The formation of the peculiar hydrolysis products may be explained by assuming that the α-oxime is first formed; this, being unstable, decomposes into hydroxylamine and the aldehyde, the latter compound being afterwards further changed in the manner shown.

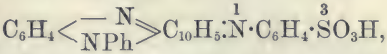
J. B. T.

The Induline Group. By O. FISCHER and E. HEPP (*Annalen*, **262**, 237—264).—*Rosindulines.*—It has been shown in a previous paper (Abstr., 1890, 908) that rosindulines are produced by the action of a large number of naphthaleneazo-derivatives, or nitrosonaphthalene derivatives on aniline or analogous bases; in the preparation of these dyes quinoneanilides, such as anilidonaphthaquinoneanil, are formed as intermediate products just as dianilidoquinonedianil (azophenine) is formed in the preparation of the blue indulines of the benzene series. In order to obtain a good yield of the rosinduline, it is not necessary to work under conditions which are favourable to the production of quinoneanilides; on the contrary, the yield is considerably larger when the quinoneanilide is obtained in only small quantities, because it is only when in the nascent state that it is readily transformed into a rosinduline. The conditions favourable to the formation of a quinoneanilide are (1) a comparatively low temperature in the fusion process, and (2) the presence of some diluent; consequently when aniline is boiled with benzeneazo-α-naphthylamine hydrochloride in glacial acetic acid solution, and when nitrosophenyl-α-naphthylamine is heated with aniline in 50 per cent. acetic acid solution, anilidonaphthaquinoneanil is formed in large quantities.

In preparing phenylrosinduline from benzeneazo-α-naphthylamine and aniline (*loc. cit.*), benzeneazo-α-phenylnaphthylamine (*loc. cit.*) is first formed; as the last-named compound dissolves in sulphuric acid yielding a blue solution, whereas the rosinduline gives a green solution, the course of the reaction can be easily followed.

Anilidoisonaphthylrosinduline, $C_{38}H_{26}N_4$, is formed in small quantities in preparing phenylrosinduline as previously described (Abstr., 1888, 1291, and 1890, 909), and remains undissolved on extracting the melt with benzene. It crystallises from hot alcoholic xylene in bronze-coloured needles, melts at a very high temperature, and is very sparingly soluble in all ordinary solvents; it dissolves in concentrated sulphuric acid yielding a green solution in which an indigo-blue, flocculent precipitate is produced on the addition of water. The *hydrochloride*, $C_{38}H_{26}N_4,HCl$, crystallises from alcohol, in which it is sparingly soluble, in bronze-coloured plates. When anilidoisonaphthylrosinduline is heated at 180—200° with a mixture of glacial acetic acid and concentrated hydrochloric acid, it is decomposed into aniline and a base of the composition $C_{26}H_{18}N_2O_2$, which is probably a hydroxy-derivative of the isonaphthylrosindone (hydroxyphenyldinaphthazine) previously described (Abstr., 1890, 910). This new base dissolves in alcoholic benzene yielding a rose-coloured solution which shows an intense orange-yellow fluorescence; its hydrochloride crystallises in green plates, is unstable, and dissolves in alcohol yielding a solution having a greenish-yellow fluorescence.

Rosindulines can be prepared from α-amidoazo-α-naphthylamine: When α-amidoazo-α-naphthylamine hydrochloride (1 part) is heated with aniline (2 parts) and aniline hydrochloride (1 part) at 150—180°, phenylrosinduline and isonaphthylrosinduline (Abstr., 1890, 908) are obtained.

Phenylrosindulinesulphonic acid,  $C_6H_4{<}\genfrac{}{}{0pt}{}{—N}{NPh}{>}C_{10}H_5{:}\overset{1}{N}\cdot C_6H_4\cdot\overset{3}{S}O_3H$, is formed when phenylrosinduline is heated at 100° with concentrated sulphuric acid; it is a red, very sparingly soluble powder. The sodium, potassium, and ammonium salts are only very sparingly soluble in boiling water, from which they crystallise in thin plates. When the acid is heated with water at 200°, it is decomposed into rosindone and metamidobenzenesulphonic acid.

Rosindone can be converted into a sulphonic acid by treating it with sulphuric anhydride; this acid dyes silk a yellowish-red shade which shows a fiery-red fluoresence, and its salts are readily soluble.

Bromorosindone, $C_{22}H_{13}N_2OBr$, is deposited in the form of a red powder on adding bromine (2 mols.) to a well-cooled glacial acetic acid solution of rosindone; it crystallises from alcoholic benzene in bright-red prisms, and is almost insoluble in cold glacial acetic acid, but more readily in alcohol and chloroform. Both bromorosindone and its sulphonic acid are eosin-coloured dyes; the shades obtained are brilliantly fluorescent. When chlorine is passed into an acetic acid solution of rosindone, the colour gradually disappears, and a colourless compound containing chlorine, probably a ketochloride, is deposited on the addition of water.

Rosindonic acid, $C_{22}H_{14}N_2O_3$, is formed when rosinduline, rosindulinesulphonic acid, or rosindone is warmed with a glacial acetic acid solution of chromic acid until the solution becomes colourless. It separates from a mixture of benzene and light petroleum in colourless crystals, melts at 209°, and is insoluble in water and only sparingly soluble in alcohol, but readily in ether and benzene; it dissolves in concentrated sulphuric acid yielding an intensely yellow solution, which becomes colourless on the addition of water. The *silver* salt, $C_{22}H_{13}N_2O_3Ag$, crystallises from hot water in shining plates; the potassium salt and the sodium salt are readily soluble in water, but the barium salt and the calcium salt are only sparingly soluble, and the copper salt and the lead salt are insoluble.

Anilidonaphthaquinonedianil, $NHPh\cdot C_{10}H_5(NPh)_2[(NPh)_2:NHPh = 1:4:2]$, is formed as an intermediate product in the oxidation of trianilidonaphthalene to phenylrosinduline by mercuric oxide (Abstr., 1890, 908); it crystallises from benzene or alcohol in orange-yellow prisms, melts at 159°, and on reduction with zinc-dust and acetic acid is converted into trianilidonaphthalene.

Quinoneanilides and Azophenines.—When orthonitrophenol (1 part) is boiled for a few hours with aniline (2 parts) in 50 per cent. acetic acid solution, a considerable quantity of dianilidoquinoneanil, identical with the compound obtained by Zincke and Hagen from quinone and aniline (*Ber.*, **18**, 788), is deposited. The compound obtained from dibromonitrosophenol and previously described by the authors as hydroxyazophenine (Abstr., 1888, 456) and the substance prepared by Kohler from paranitrosometahydroxydiphenylamine (Abstr., 1888, 587) are both identical with Zincke and Hagen's dianilidoquinoneanil.

Toluazophenine, $C_6H_2(NC_7H_7)_2(NHC_7H_7)_2$ $[(NC_7H_7)_2 : (NHC_7H_7)_2 = 1 : 4 : 2 : 5]$, was first prepared by Kimich (*Ber.*, **8**, 1031), who erroneously assigned to it the composition $C_{40}H_{37}N_5O$; when boiled with methyl alcohol and concentrated sulphuric acid, it is decomposed into paratoluidine and diparatoluidoquinone.

The compound prepared by Nölting and Witt (*Ber.*, **17**, 82) from orthamidoazotoluene and paratoluidine has the composition $C_{35}H_{34}N_4$ and not $C_{42}H_{41}N_5$; when boiled with methyl alcohol and concentrated sulphuric acid, it is decomposed into *ditoluidotoluquinone*, $C_6HO_2Me(NHC_7H_7)_2$, and paratoluidine. This ditoluidotoluquinone, crystallises from alcohol in brown needles, melts at 178°, and is isomeric with the symmetrical compound (m. p. 241°) previously obtained by the authors from toluquinone and paratoluidine (Abstr., 1890, 912); its constitution is, therefore, represented by one of the two formulæ $[Me : O_2 : (NHC_7H_7)_2 = 1 : 2 : 5 : 3 : 4$ or $= 1 : 2 : 5 : 4 : 6]$, so that the original compound of the composition $C_{35}H_{34}N_4$ is an *azotoline* of the constitution

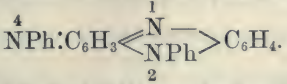
$$[Me : (NC_7H_7)_2 : (NHC_7H_7)_2 = 1 : 2 : 5 : 3 : 4, \text{ or } = 1 : 2 : 5 : 4 : 6].$$

The compound of the composition $C_{18}H_{14}N_2O_2$, obtained by Fèvre (Abstr., 1883, 734) from nitrosoresorcinol and aniline, is probably a hydroxyanilidoquinoneanil of the constitution $[O : OH : NPh : NHPh = 1 : 3 : 4 : 6]$; when boiled with methyl alcohol and sulphuric acid, it is decomposed into aniline and a crystalline compound of the composition $C_{13}H_{11}NO_3$, which melts at 189°, and is probably methoxyanilidoquinone.

Benzeneindulines.—Amidoazobenzeneinduline, (Abstr., 1890, 764) melts at 125°. The *hydrochloride*, $C_{18}H_{13}N_3,HCl$, crystallises in brownish-red prisms; the *hydrobromide*, $C_{18}H_{13}N_3,HBr$, crystallises in yellow, lustrous needles and is rather sparingly soluble in water. The *nitrate*, $C_{18}H_{13}N_3,HNO_3$, is a bronze-coloured, crystalline powder which dissolves in water yielding a reddish-violet solution.

Amidophenylinduline, the preparation of which is described in the German patent, No. 50,534, crystallises from alcohol or benzene in greenish prisms, melts at 150—152° (not at 255—260° as stated in the patent), and is only sparingly soluble in benzene; the hydrochloride is very sparingly soluble in water. The *nitrate*, $C_{24}H_{18}N_4,HNO_3$, crystallises in green, and the *aurochloride*, $C_{24}H_{18}N_4,HAuCl_4$, in bronze-coloured plates. When the base is heated with concentrated hydrochloric acid at 150°, it is decomposed into ammonia, aniline, and a hydroxy-compound which is only very sparingly soluble in alcohol, yielding a reddish-violet solution.

Phenylinduline, $C_{24}H_{17}N_3$, is obtained when amidophenylinduline is diazotised in alcoholic solution, the solution of the product heated to boiling, diluted with water, and the base precipitated with ammonia. It crystallises from a mixture of methyl alcohol and benzene in thick, red plates, melts at 230—231°, and is readily soluble in benzene, but only sparingly in methyl alcohol, and almost insoluble in light petroleum; it dissolves in concentrated hydrochloric acid and sulphuric acid with a blue, in dilute mineral acids with a bluish-violet, and in acetic acid with a red coloration. The hydrochloride and the sulphate crystallise in green prisms.

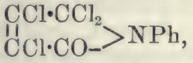
Further investigation has shown that the compound (m. p. 229—230°) obtained by heating azophenine with concentrated hydrochloric acid, and which was first thought to be anilidoquinonedianil, $C_{24}H_{19}N_3$ (Abstr., 1890, 912), is identical with the phenylinduline just described; this fact shows that phenylinduline must have the constitution  $\overset{4}{N}Ph{:}C_6H_3{<}\begin{matrix}\overset{1}{N}-\\ \underset{2}{NPh}\end{matrix}{>}C_6H_4$. The benzeneindulines are, therefore, like the rosindulines, derivatives of paraquinone, whereas the saffranines and eurhodines are derivatives of orthoquinone.

The blue compound obtained by boiling amidoazobenzene hydrochloride with aniline hydrochloride in aqueous solution contains oxygen, and does not belong to the same class of compounds as the indulines.

Indazine, a blue dye obtained by treating nitrosodimethylaniline with diphenylmetaphenylenediamine, is the hydrochloride of a base which has many properties in common with the saffranine bases, but which, like the indulines, is free from oxygen; the free base, $C_{26}H_{22}N_4$, crystallises from benzene in compact bronze-coloured prisms, melts at 218—220°?, and effloresces on exposure to the air owing to loss of benzene. It is readily soluble in alcohol and benzene, but only sparingly in ether, light petroleum, and hot water, and insoluble in alkalis; it dissolves in concentrated sulphuric acid yielding a green solution which turns yellow on the addition of water. The hydrochloride and the sulphate dissolve freely in water giving bluish-violet solutions, but the nitrate is only sparingly soluble.

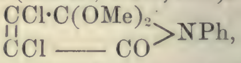
Nitrosoaniline combines with diphenylmetaphenylenediamine forming a violet indazine; nitrosodiphenylamine and the meta-base give a blue compound. F. S. K.

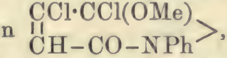
Dichloromaleïnanil Chloride. By R. Anschütz and C. Beavis (*Annalen*, **263**, 156—163).—*Dichloromaleïnanil chloride*,



$$\begin{matrix}CCl{\cdot}CCl_2\\ \|\\ CCl{\cdot}CO-\end{matrix}{>}NPh,$$

is easily obtained in a pure condition by heating succinanil (1 mol.) with phosphorus pentachloride (4 mols.) at 130°, until the reaction is at an end, and then distilling the product under greatly reduced pressure. It crystallises from light petroleum and glacial acetic acid in colourless, transparent prisms, melts at 123—124°, boils at 179° under a pressure of about 11 mm., and is very readily soluble in chloroform, carbon bisulphide, and acetone; when treated with boiling water, it is gradually converted into dichloromaleïnanil (m. p. 203°), the compound which Kauder considered to be produced directly by the action of phosphorus pentachloride on succinanil (Abstr., 1885, 651).

Dichloromaleïnanil dimethyl ether,  $\left.\begin{array}{l}\mathrm{CCl{\cdot}C(OMe)_2}\\ \Vert\\ \mathrm{CCl\text{ —— }CO}\end{array}\right>\mathrm{NPh}$, is deposited in colourless needles, when the preceding compound is dissolved in warm alcohol, and the solution then allowed to cool; it melts at 110° and is gradually converted into dichloromaleïnanil when boiled with a mixture of methyl alcohol and hydrochloric acid. The corresponding *diethyl* ether, $C_{14}H_{15}Cl_2NO_3$, crystallises from alcohol in colourless, lustrous prisms, melts at 96—97°, and is converted into dichloromaleïnanil by boiling alcoholic hydrochloric acid.

A compound of the composition $C_{11}H_9Cl_2NO$, which has possibly the constitution  $\left.\begin{array}{l}\mathrm{CCl{\cdot}CCl(OMe)}\\ \Vert\\ \mathrm{CH{-}CO{-}NPh}\end{array}\right>$, is formed when succinanil (1 mol.) is warmed with phosphorus pentachloride and the product treated with methyl alcohol; it melts at 91°. F. S. K.

Formation of Thianhydro-compounds. By P. Jacobson and A. Frankenbacher (*Ber.*, **24**, 1400—1411).—Amidophenylmercaptomethylmercaptan, $C_6H_4<\genfrac{}{}{0pt}{}{N}{S}>C{\cdot}SH$, which was first obtained by Hofmann, may be prepared by heating azobenzene with 2·5 parts of carbon bisulphide in a sealed tube for five hours at 260—270°; the product is purified by solution in soda and crystallisation from alcohol; the yield is 60 per cent. of the azobenzene employed. It is proposed to term the compound *thiocarbamidothiophenol;* its formation is probably preceded by a decomposition of the azobenzene and carbon bisulphide into phenylthiocarbimide and sulphur; these, however, combine to form the unstable intermediate product $SH{\cdot}C_6H_4{\cdot}N{:}CS$, from which the thiophenol is obtained by intramolecular rearrangement; this theory is supported by the fact that the thiophenol may be prepared by the direct interaction of sulphur and phenylthiocarbimide at 260—270°. The thiophenol does not react with aniline, and yields no acetyl derivative; the *mercurochloride*, $C_7H_5NS_2,HgCl_2$, is colourless and crystalline.

Thiocarbamidothionaphthol is prepared in a similar manner by heating α-naphthylthiocarbimide with sulphur for 4—5 hours at 220—230°; it is identical with the compound formed by the action of carbon bisulphide on diamidodinaphthyl bisulphide; on oxidation, the corresponding bisulphide is formed, together with a small quantity of a second compound which crystallises from benzene in plates, and melts at 180°; it is isomeric with the first compound, and is probably derived from a 1-1′-thiocarbamidonaphthol. The *mercurochloride* is deposited in transparent, tabular crystals melting at 209—210°.

β-Naphthylthiocarbamide reacts with sulphur in a similar manner to the α-derivative; the product is represented by the formula $C_{10}H_6<\genfrac{}{}{0pt}{}{N}{S}>C{\cdot}SH$ [N : S = 3 : 4 or 3 : 2], the former positions being the more probable: it crystallises in small needles, and melts at 232° with decomposition.

The *bisulphide*, $C_{10}H_6{<}\substack{N\\S}{>}C\cdot S_2\cdot C{<}\substack{N\\S}{>}C_{10}H_6$, prepared by oxidation of the preceding compound with potassium ferricyanide in alkaline solution, is deposited from benzene in prismatic crystals and melts at 180°; on boiling with alcoholic potash, the thionaphthol is regenerated. No crystalline mercurochloride could be obtained.

The *methyl ether*, $C_{10}H_6{<}\substack{N\\S}{>}C\cdot SMe$, is formed by heating the thionaphthol with methyl iodide, and crystallises from dilute alcohol in colourless needles melting at 73·5—74°.

Carbanilamidothiophenol, $C_6H_4{<}\substack{N\\S}{>}C\cdot NHPh$, is prepared by heating azobenzene with two molecular proportions of phenylthiocarbimide for three hours at 260—270°; the product is most readily purified by solution in light petroleum or hydrochloric acid. The *picrate* crystallises from alcohol, and melts at 222°. The *aurochloride* forms brownish-red needles. The *acetyl derivative* is deposited from alcohol in colourless needles and melts at 167°. J. B. T.

Action of Sulphur on Benzaldehyde. By G. A. BARBAGLIA and A. MARQUARDT (*Ber.*, **24**, 1881—1883).—When benzaldehyde (30 grams) is heated with sulphur (10 grams) in a sealed tube for 36 hours (compare Gazzarini, Abstr., 1888, 950), a reddish-coloured, crystalline mass, consisting of small, lustrous plates and rectangular prisms, is obtained. On opening the tube, little or no hydrogen sulphide is given off. The product is treated with ether, whereby the crystals are dissolved, leaving the sulphur and another compound (see below) behind. The ethereal solution is shaken with an aqueous solution of sodium carbonate, and on acidifying the alkaline extract with hydrochloric acid, a copious precipitation of benzoic acid occurs, whilst, on evaporating the ethereal solution, a compound is obtained which, on repeated crystallisation from alcohol, forms lustrous, white plates, and melts at 121—122°; it is identified as stilbene by its melting point, and that of the dibromide obtained from it. The residue insoluble in ether yields, on treatment with benzene or chloroform, a compound containing sulphur, crystallising in white needles, and melting at 164—167°, which has all the properties of γ-thiobenzaldehyde (Baumann and Fromm, Abstr., 1890, 25). It therefore appears probable that the initial action of sulphur on benzaldehyde is the formation of thiobenzaldehyde and benzoic acid, being in this stage analogous to the formation of thio-derivatives with aldehydes of the fatty series (see Abstr., 1881, 34; 1885, 136), the thiobenzaldehyde then decomposing into stilbene and sulphur thus: $2CHSPh = CHPh{:}CHPh + S_2$. In this case, the formation of stilbene ought to be effected by very small quantities of sulphur, and experiment shows that a quantity of the latter equal in weight to $\frac{1}{10}$ of the benzaldehyde is sufficient. Klinger (Abstr., 1877, 306; 1878,

132) obtained stilbene by heating amorphous thiobenzaldehyde with copper powder. A. R. L.

Thio-derivatives of Benzaldehyde. By E. BAUMANN and E. FROMM (*Ber.*, **24**, 1431—1440).—The majority of thioaldehydes do not volatilise without decomposition, and are very sparingly soluble in benzene or glacial acetic acid; molecular weight determinations of them are therefore most conveniently made with naphthalene as solvent. The molecular depression for naphthalene is given by Raoult as 82, by Fabinzi as 85·6, whilst Eykmann found it to vary from 68·3 to 76·6, although for the greater number of his experiments the value is about 70. The theoretical number deduced from Van't Hoff's formula is 69·4. The authors have determined the molecular depression in the case of trithioformaldehyde, α- and β-trithiacetaldehyde, and trimethylene tetrasulphide, the vapour densities of which are known; the highest value was 72, the lowest 67·7, and the mean 69·6; the molecular weights thus obtained agree closely with those calculated from the depression in glacial acetic acid solution.

β-Thiobenzaldehyde (m. p. 225—226°) has the formula $3(C_7H_6S)$, and crystallises with 1 mol. benzene; on account of its analogy with β-thiacetaldehyde, its present name is correct (compare this vol., p. 1008). γ-Thiobenzaldehyde (m. p. 167°) also has a trimolecular formula; it is proposed in future to term it α-thiobenzaldehyde to show its relation to α-thiacetaldehyde.

The compound hitherto called α-thiobenzaldehyde, which is amorphous, melts at 83—85°, and is prepared by the action of ammonium sulphide, or hydrogen sulphide, on benzaldehyde, is not a trithiobenzaldehyde, but a complicated polymeride, or perhaps a mixture of several compounds of high molecular weight; its formula is probably $(C_7H_6S)_{12}$, and it is comparable with the polymeric thioformaldehyde of Wohl.

By repeated solution of this amorphous compound, a small quantity of β-thiobenzaldehyde is separated; the remainder, however, is quite unchanged in properties. The elementary analyses of several preparations give 0·3 to 1·0 per cent. more sulphur than is required by the formula $(C_7H_6S)_x$, the carbon being correspondingly low; this may be due to the presence of a little free sulphur.

Thiobenzaldine is obtained in small quantity during the preparation of polymeric benzaldehyde by the interaction of ammonium sulphide and benzaldehyde.

The formation of the polymeric compound is preceded by that of a hydroxymercaptan, OH·CHPh·SH, which is much less stable than the corresponding formic and acetic derivatives, and immediately undergoes condensation, the solvent alcohol probably acting as a dehydrating agent. The two trithiobenzaldehydes are odourless; the polymeric compound, when recently prepared, has a strong smell, which gradually disappears as purification proceeds. J. B. T.

Aromatic Thioaldehydes. By E. BAUMANN and E. FROMM (*Ber.*, **24**, 1441—1456; compare this vol., p. 1008.).—*α-Trithioparamethoxybenzaldehyde*, $C_{24}H_{24}S_3O_3$, is prepared by dissolving the aldehyde in alcohol, adding 0·1 part of hydrochloric acid, and saturating the solution with hydrogen sulphide at a temperature of −5° to −10°; it is readily soluble in benzene, sparingly in alcohol, and is deposited in small, needle-shaped crystals melting at 127°. The corresponding β-derivative is formed in a similar manner in presence of excess of hydrochloric acid and at ordinary temperatures; it crystallises with 1 mol. benzene in transparent plates, and melts at 183°.

By the action of hydrogen sulphide on paramethoxybenzaldehyde in alcoholic solution, a plastic compound is obtained which hardens after some time; it softens at 75—77°, and contains more sulphur than the thioaldehydes.

On treatment of the methoxybenzaldehyde, in alcoholic solution, with ammonium sulphide, a crystalline polymeric thio-derivative of the formula $(C_8H_8SO)_x$ is obtained, melting at 90—92°, together with *anisyl bisulphide*, $S_2(CH_2{\cdot}C_6H_4{\cdot}OMe)_2$; this crystallises from alcohol, on the addition of water, in large, thin plates. By the reduction of this compound, *anisylmercaptan* is formed; it is a yellow, oily liquid, volatile with steam. The *copper* and *silver salts* are yellow and amorphous.

α-Trithiorthomethoxybenzaldehyde is prepared in a similar manner to the above para-compound, which it closely resembles, and melts at 157°. The *β-derivative* crystallises from benzene in slender needles, and melts at 224°. From the mother liquors, an amorphous substance is deposited which softens at 60°, and melts at about 70°; it is probably a mixture of oxysulphides. An impure product is obtained by the action of hydrogen sulphide on the methoxybenzaldehyde; the compound formed with ammonium sulphide is a mixture of various polymerides, and melts at 85—88°.

Orthisobutoxybenzaldehyde is a strongly refractive liquid which boils at 265°. The *α-trithioaldehyde*, $C_{33}H_{42}S_3O_3$, is readily soluble, crystallises from alcohol in slender needles, and melts at 142°. The *β-modification* is deposited from benzene in transparent plates or prisms, and melts at 162—163°. As in the preceding cases, the polymeric compounds are impure; that obtained with ammonium sulphide melts at 52—56°, and contains more sulphur than the thioaldehydes.

α-Trithiocinnamaldehyde, $C_{27}H_{24}S_3$, crystallises from alcohol and melts at 167°; it is readily converted into the isomeric form by the action of ethyl iodide, but iodine does not cause this change. The *β-compound* is deposited in small, prismatic crystals, which do not contain benzene of crystallisation, and melt at 213°. On treatment of cinnamaldehyde in alcoholic solution with hydrogen sulphide, a yellow, viscid liquid is formed which contains oxygen, and consists of a mixture of several compounds. With ammonium sulphide and cinnamaldehyde, a colourless, flocculent precipitate is obtained which does not crystallise; it softens at 127°, and melts at 142°, and, on analysis, proves to be a mixture of at least two substances, one containing nitrogen, and the other more sulphur than the trithioaldehydes; the molecular weight is not less than 722°.

The molecular weights of all the above compounds were determined by Raoult's method in naphthalene solution.

These results show that in every case hitherto investigated aromatic aldehydes yield two isomeric trithio-derivatives, together with substances which are either mixtures or else complicated polymerides; the stability of these tri-derivatives shows that the sulphur atoms are each linked to two carbon atoms, or, in other words, that the compounds are to be regarded as trithiomethylene substitution products.

The tri- and poly-thiobenzaldehydes yield cinnamene and thionessal on heating; lepiden, the corresponding oxygen compound, has been shown by Japp and Klingemann to be tetraphenylfurfuran. Thionessal is therefore tetraphenylthiophen, and its formation, by heating cinnamene or phenylacetic acid with sulphur is an additional proof of the correctness of this view. J. B. T.

Behaviour of Cinnamaldehyde towards Alkaline Hydrogen Sulphites. By F. HEUSLER (*Ber.*, **24**, 1805—1807).—The reaction which takes between cinnamaldehyde and alkaline hydrogen sulphites was first examined by Bertagnini (*Annalen*, **85**, 271), and has been utilised by Bertram and Gildemeister for estimating the quantity of cinnamaldehyde in oil of cassia. The author finds that cold saturated solutions of potassium and sodium hydrogen sulphites combine with cinnamaldehyde in the normal manner, the last-named forming the compound $CHPh\colon CH\cdot CH(OH)\cdot SO_3Na$, which then, on heating, undergoes the following reaction :—

$$2CHPh\colon CH\cdot CH(OH)\cdot SO_3Na = CHPh\colon CH\cdot CHO + C_2H_3Ph(SO_3Na)\cdot CH(OH)\cdot SO_3Na.$$

This compound may also be obtained directly, and in quantitative proportions, by adding cinnamaldehyde (1 mol.) to a hot concentrated solution of an alkaline hydrogen sulphite. The *potassium* salt crystallises from water in compact needles, having the composition $C_9H_{10}O(SO_3K)_2 + 2H_2O$; and on dry distillation or boiling with soda is reconverted into cinnamaldehyde. Dilute sulphuric acid, on the other hand, converts it into cinnamaldehydesulphonic acid, $C_2H_3Ph(SO_3H)\cdot CHO$, which readily combines with phenylhydrazine, forming the *phenylhydrazine salt of cinnamaldehydrazonesulphonic acid*; this compound crystallises in yellowish plates, melts with decomposition at 165—166°, and is decomposed by aqueous soda with formation of phenylhydrazine and cinnamaldehydrazone. H. G. C.

Some Ketones. By G. ERRERA (*Gazzetta*, **21**, 94—103).—*Paratolyl ethyl ketone*, $C_6H_4Me\cdot COEt$, prepared by the dry distillation of a mixture of barium propionate and paratoluate, is a pale-yellow liquid with a characteristic odour, which boils at 237—239°, and is insoluble in water. It does not combine with sodium hydrogen sulphite, but it yields a liquid condensation product with phenylhydrazine; it also yields an *oxime*, which crystallises in large, colourless plates melting at 86—87°. On oxidation with nitric acid (sp. gr. = 1·38), dinitroethane and metanitroparatoluic acid are formed. *Metanitroparatolyl ethyl ketone*, $NO_2\cdot C_6H_3Me\cdot COEt$, prepared by dissolving paratolyl ethyl ketone in well cooled nitric acid (sp. gr. = 1·51) and precipitating with water, crystallises from alcohol in pale-yellow plates which melt at 50—51°. On boiling with dilute nitric acid, it is converted into metanitroparatoluic acid. It yields a *phenylhydrazone*,

$$NO_2\cdot C_6H_3Me\cdot CEt\colon N_2HPh,$$

which crystallises from alcohol in orange-coloured needles melting at 147—149°. *Metadinitrodiparatolyl ketone*, $CO(C_6H_3Me\cdot NO_2)_2$, is obtained by the action of nitric acid (sp. gr. 1·51) on diparatolyl ketone. It dissolves freely in warm alcohol, and crystallises, on cooling, in yellow, prismatic needles. It is not affected by prolonged boiling with ordinary nitric acid, and is only very slowly and partially decomposed by the strong acid (1·45). *Diparatolyl ketone*, $CO(C_6H_4Me)_2$, is obtained as a bye-product in the preparation of ethyl paratolyl ketone, or by the action of aluminium chloride on a mixture of toluene and carbonyl chloride. It yields, with some difficulty, an *oxime*, $NOH\colon C(C_6H_4Me)_2$, which crystallises in colourless prisms melting at 161—162°.

Paraxylyl methyl ketone, $C_6H_4Me\cdot CH_2\cdot COMe$, is prepared by distilling a mixture of the barium salts of acetic acid and homoparatoluic acid ($C_6H_4Me\cdot CH_2\cdot COOH$, from synthetical paraxylene), and treating the fraction 220—250° with sodium hydrogen sulphite. It is a colourless, aromatic liquid, boiling at 232—233°. It yields an oily phenylhydrazone and an *oxime*, which crystallises in large, oblique prisms melting at 90—91°. The *metanitro-derivative* is obtained in an impure condition by the action of nitric acid (1·51) on the ketone; the *hydrazone*, $NO_2\cdot C_6H_3Me\cdot CH_2\cdot CMe\colon N_2HPh$, crystallises from alcohol in long, brilliant-red needles melting at 212—213°.

Diparaxylyl ketone, $CO(CH_2\cdot C_6H_4Me)_2$, is obtained in the preparation of paraxylyl methyl ketone, occurring among the products which distil over above 300°. It forms colourless crystals melting at 54°. The *oxime*, $NOH\colon C(CH_2\cdot C_6H_4Me)_2$, crystallises in colourless needles and melts at 106°.

S. B. A. A.

Hydrogenation of Benzoic Acid. By O. Aschan (*Ber.*, **24**, 1864—1869).—On reduction of benzoic acid with sodium amalgam in acid solution, in addition to benzaldehyde and benzyl alcohol, about 8 per cent. of tetrahydrobenzoic acid is formed. Better results are obtained by dissolving 50 grams of benzoic acid in 250 c.c. of 10 per cent. soda solution in a reflux apparatus; 2·5 kilos. of sodium amalgam are added in portions of 300—400 grams, and the flask is heated on the water-bath for 20—25 hours, a slow, continuous stream of carbonic anhydride being passed into the liquid; sufficient water must be added from time to time in order to prevent the separation of any sodium salts. The yield is 60—70 per cent.; but to attain this it is needful that the amalgam should be quite pure. Tetrahydrobenzoic acid behaves in every respect like an unsaturated compound; on treatment with bromine in molecular proportions, two *dibromides* are formed; the one obtained in larger quantity crystallises from a mixture of benzene and light petroleum, melts at 163°, and on warming with soda is converted into a crystalline substance, which is probably a bromolactone. The second compound is soluble in light petroleum, crystallises in long needles, and yields a solid, unsaturated acid on treatment with soda. Tetrahydrobenzoic acid combines directly with hydrogen iodide and hydrogen bromide; by the action of sodium amalgam on the latter product, hexahydrobenzoic acid is formed as a viscid liquid, together with a small quantity of a solid acid. The *calcium salt* crystallises in long prisms, with $4H_2O$; the *silver salt* is amorphous. On heating tetrahydrobenzoic acid with concentrated hydriodic acid at 220—240°, a solid acid, free from iodine, is formed, and is being further investigated. *Methyl tetrahydrobenzoate* boils at 185—187°, and gradually undergoes decomposition. On hydrolysis with alcoholic potash, the sparingly soluble salt of a new acid is formed, crystallising in large plates. The acid itself melts above 100°, and will be described later.

It appears probable that hexahydrobenzoic acid will prove to be identical with hexanaphthenecarboxylic acid. J. B. T.

Asymmetrical Phenylhydrazidoacetic Acid. By A. REISSERT and W. KAYSER (*Ber.*, **24**, 1519—1522; see also Abstr., 1884, 1152). —The *ethyl salt* of *asymmetrical phenylhydrazidoacetic acid*,

$$NH_2{\cdot}NPh{\cdot}CH_2{\cdot}COOEt,$$

may be obtained by heating together phenylhydrazine (2 mols.) and ethyl chloracetate (1 mol.) at 100° for 2—3 hours, dissolving the product in dilute hydrochloric acid, and extracting the solution with ether. The mass remaining on evaporating off the latter, is spread on a porous plate, and the residue recrystallised from benzene. It forms white needles, melts at 127°, is readily soluble in alcohol, ether, and chloroform, more sparingly in benzene, and is almost insoluble in light petroleum and water. The yield is small, owing to secondary reactions.

The ethyl salt is readily decomposed by dilute aqueous soda, with formation of *asymmetrical phenylhydrazidoacetic acid*,

$$NH_2{\cdot}NPh{\cdot}CH_2{\cdot}COOH,$$

which separates, on addition of acids, as a yellow, woolly, unstable precipitate. It is purified by dissolving repeatedly in boiling water and cooling quickly, when it forms slender, yellowish needles; it becomes brown at 125°, and melts with decomposition at 130—131°. It is soluble in most of the usual solvents, and only reduces Fehling's solution on warming. It differs altogether from the symmetrical phenylhydrazidoacetic acid described by Elbers (Abstr., 1885, 535), and must, therefore, be the asymmetrical compound. H. G. C.

Anilpyruvic Acid. By C. BÖTTINGER (*Annalen*, **263**, 125—128). —*Tribromodianilidopyruvic acid*, $C_{15}H_{13}Br_3N_2O_2$, is obtained when anilpyruvic acid (5 grams) is suspended in chloroform, treated with bromine (6 grams) at the ordinary temperature, the dry product shaken with dilute soda to free it from brominated aniline, and the filtered solution acidified with hydrochloric acid; it crystallises from boiling alcohol, in which it is moderately easily soluble, in slender, colourless needles, melts at 264° with decomposition, has an intensely bitter taste, and is not decomposed by boiling soda. It dissolves in concentrated hydrochloric acid and in concentrated sulphuric acid with a yellow coloration, and it is slowly decomposed by concentrated hydrochloric acid at 225° with evolution of carbonic anhydride; when treated with sodium amalgam, it loses bromine, and is converted into substances which are readily soluble in dilute acids. The *silver* salt is a colourless compound, soluble in ammonia. F. S. K.

Action of an Alcoholic Solution of Silver Nitrate on Ethyl Phenyldibromopropionate. By L. P. Kinnicutt and G. D. Moore (*Amer. Chem. J.*, **13**, 204—205).—It has been already noticed (Abstr., 1885, 1010) that an alcoholic solution of silver nitrate only removes 1 atom of bromine from an alcoholic solution of ethyl phenyldibromopropionate. If the alcoholic solution is poured off from the settled silver bromide into water, an oil separates; this is extracted by ether and dried over calcium chloride; analysis shows that it is ethyl phenyl-α-bromo-β-nitropropionate,

$$NO_2{\cdot}CHPh{\cdot}CHBr{\cdot}COOEt,$$

its orientation being settled by the facts that it yields benzaldehyde on oxidation, and bromocinnamic acid (m. p. 131°) on treatment with sodium hydroxide. It is a pale straw-coloured oil of sweetish odour, and soluble in alcohol and ether; it does not distil without decomposition. The subject is still being investigated.

A. G. B.

Derivatives of Cumic Acid. By M. Fileti and F. Crosa (*Gazzetta*, **21**, 28—40).—*Metabromocumic acid*, $C_6H_3BrPr{\cdot}COOH$ [COOH : Br : Pr = 1 : 3 : 4], previously described by Naquet and Louguinine (*Compt. rend.*, **72**, 1031), and by Gerichten (Abstr., 1879, 230), may be prepared directly from cumic acid and bromine. It separates from dilute alcohol in large, white crystals, melts at 150—151°, and is identical with the acid obtained by the authors from bromocymene prepared from thymol. The *magnesium* salt, $(C_{10}H_{10}BrO_2)_2Mg + 8H_2O$, crystallises in long, silky needles which become anhydrous at 160°. It is soluble in hot water. The *methyl* salt is an oily liquid which decomposes on distillation. The *acid chloride* is also a liquid, and decomposes on heating. The *amide*, $C_9H_{10}Br{\cdot}CONH_2$, crystallises from benzene in silky needles, melts at 103—104°, and dissolves freely in alcohol and ether.

Orthonitrobromocumic Acid,

$$NO_2{\cdot}C_6H_2BrPr{\cdot}COOH\ [COOH : Br : Pr : NO_2 = 1 : 3 : 4 : 6].$$

—Bromocumic acid on nitration yields a mixture of three acids which may be separated by fractional crystallisation from benzene; they are probably the three isomeric nitrobromocumic acids theoretically possible. The acid [NO_2 = 6] crystallises from benzene in large, pale-yellow, rhombic prisms, melts at 138—139°, and dissolves in alcohol, ether, &c. The *ammonium* salt, $C_{10}H_9BrNO_4{\cdot}NH_4$, forms large, yellow plates very soluble in alcohol. The *magnesium* salt,

$$(C_{10}H_9BrNO_4)_2Mg + 4H_2O,$$

crystallises in thin, pale-yellow, lustrous plates which become anhydrous at 200°. It is very soluble in hot water. On reducing the acid with sodium amalgam, Widman's orthamidocumic acid (Abstr., 1886, 466) is formed, thus indicating the ortho-position of the NO_2 group.

Orthamidometabromocumic acid, prepared by treating a mixture of the nitro-derivative and ammonia with ferrous sulphate, crystallises from dilute alcohol in long, shining, pale-brown needles, melts at 166—167°, and dissolves freely in alcohol and ether, but only sparingly in water.

Paradibromocumic Acid, $C_6H_2Br_2Pr{\cdot}COOH$ [$COOH : Br : Pr : Br = 1 : 3 : 4 : 6$].—When the preceding amido-acid is diazotised, the product crystallises in minute, rhombic prisms, which melt at 134° if gently raised to that temperature, but explode if sharply heated. Paradibromocumic acid, prepared by dissolving this diazoamido-compound in a saturated solution of hydrobromic acid, crystallises from light petroleum in triclinic prisms, melts at 148—149° with previous softening, and dissolves in alcohol, ether, and benzene. On oxidation with dilute nitric acid (sp. gr. 1·06), it yields paradibromoterephthalic acid, a confirmation of the constitutional formulæ assigned to some of the preceding compounds.

Paradibromonitrocumic acid, $NO_2{\cdot}C_6HBr_2Pr{\cdot}COOH$, prepared by nitrating dibromocumic acid, crystallises from very dilute alcohol in brilliant, yellow scales, melts at 199—200°, and dissolves very freely in benzene and alcohol.

Paradibromonitroterephthalic acid, $NO_2{\cdot}C_6HBr_2(COOH)_2$, prepared by heating dibromocumic acid with nitric acid (sp. gr. 1·2) for eight hours at 180°, crystallises from its aqueous solution in thin, slightly yellowish plates, melts at 257—258°, and dissolves in alcohol and in boiling water.

Orthonitrometabromocumic acid [$COOH : NO_2 : Br : Pr = 1 : 2 : 3 : 4$] is obtained, together with the acid [$NO_2 = 6$], as mentioned above. It crystallises from benzene in white needles, melts at 238—239°, dissolves readily in benzene, alcohol, and ether, but is insoluble in water. The *ammonium* salt, $C_{10}H_9BrNO_4{\cdot}NH_4$, crystallises in long, anhydrous needles, and is very soluble in water. On reduction with sodium amalgam, it yields the same orthamidocumic acid as the acid [$NO_2 = 6$]; it is therefore an ortho-acid, and the constitution assigned it is the only possible one.

Orthamidometabromocumic acid, prepared by reducing the preceding acid with ferrous sulphate, crystallises in colourless or pale pinkish, pyramidal prisms, melts at 173—174°, and dissolves in alcohol and ether, but only very sparingly in water.

Orthodibromocumic Acid.—By diazotising the preceding acid, a diazo-compound is formed, crystallising in colourless, ill-defined prisms which melt with decomposition if gradually warmed to 120° in a capillary tube, but explode on quickly heating. On treatment with hydrobromic acid, it yields the corresponding dibromocumic acid, which crystallises from light petroleum in pale, reddish-yellow, orthogonal prisms, melts at 128—129°, and dissolves freely in alcohol, ether, &c. It undergoes oxidation with great difficulty.

Orthodibromonitroterephthalic acid, $NO_2{\cdot}C_6HBr_2(COOH)_2$, prepared by oxidising the preceding acid with very dilute nitric acid (sp. gr. = 1·06 or 1·12), crystallises from boiling water in pale, yellowish plates, softens at 275°, and melts at 280—281°, decomposing as soon as it is liquefied. It is soluble in alcohol.

Metanitrometabromocumic acid [$COOH : Br : Pr : NO_2 = 1 : 3 : 4 : 5$] is the most soluble of the acids obtained by nitrating metabromocumic acid, and remains in the mother liquor after separation of the ortho-acids. It crystallises in white needles, melts at 159—160°, and dissolves very freely in benzene and alcohol. S. B. A. A.

Homocumic and Homoterephthalic Acids. By M. FILETI and G. BASSO (*Gazzetta*, **21**, 52—64).—*Homocumic acid*,

$$C_6H_4Pr{\cdot}CH_2{\cdot}COOH,$$

obtained by Rossi (*Compt. rend.*, **52**, 403) by the action of potash on cumyl cyanide, is more advantageously prepared by reducing phenylisopropylglycollic acid with tin and fuming hydrochloric acid. It crystallises from an aqueous solution in slender needles, melts at 51—52°, and dissolves readily in most solvents, but only very sparingly in water. The *barium salt*, $(C_{11}H_{13}O_2)_2Ba,4H_2O$, crystallises in vitreous, lamellar prisms; the *calcium salt* forms microscopic plates containing 3 mols. H_2O. The *magnesium salt* separates in nodules containing 4 mols. H_2O; it is more soluble than the preceding salts. The *methyl* salt is a liquid boiling at 255—257°; the *ethyl* salt boils at 264—265°. The *chloride* is a heavy liquid readily decomposed by cold water; the *amide* crystallises from boiling benzene in thin, octagonal plates, melts at 170°, and dissolves readily in alcohol, moderately in benzene, but very sparingly in ether, and not at all in water. In the preparation of the amide, there was obtained a very small quantity of a compound crystallising in oblique, acicular prisms, and melting at 104—107°, but not further investigated. The *anilide* of homocumic acid crystallises from light petroleum in plates, melts at 104°, and dissolves readily in all solvents except water.

Paradibromohomocumic acid, $C_6H_2PrBr_2{\cdot}CH_2{\cdot}COOH$, prepared by the action of bromine on homocumic acid, crystallises from light petroleum in plates, melts at 92°, and dissolves freely in all solvents but water. The *barium salt* crystallises in acicular prisms containing 5 mols. H_2O; the *magnesium salt* forms plates with 8 mols. H_2O; it is more soluble than the barium salt. The *methyl* salt is a liquid boiling without decomposition at 325—326°; the *chloride* is a heavy, colourless liquid; the *amide* crystallises from dilute alcohol in brilliant plates melting at 153°. It is insoluble in water. On oxidation with potassium permanganate, paradibromohomocumic acid is converted into dibromocumic acid and into an acid which has a percentage composition corresponding with the formula $C_{10}H_{10}Br_2O_3$; this crystallises from dilute alcohol in oblique prisms, melts at 214—215°, and probably has the constitution of a hydroxypropyldibromobenzoic acid,

$$OH{\cdot}CMe_2{\cdot}C_6H_2Br_2{\cdot}COOH\ [COOH : Br : CMe_2{\cdot}OH : Br = 1 : 2 : 4 : 5].$$

Homoterephthalic acid, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}COOH$ [1 : 4], prepared by oxidising homocumic acid with dilute nitric acid, crystallises from an aqueous solution in needles or plates, melts at 237° with partial sublimation, dissolves readily in boiling water or alcohol, but only very sparingly in other solvents. The substance described by Paternò and Spica (Abstr., 1878, 296) as homoterephthalic acid seems to have been nothing but impure terephthalic acid. The *barium* salt, $C_9H_6O_4Ba + H_2O$, becomes anhydrous at 150°; it is soluble in water. The *methyl* salt boils at 300—302°, and the *ethyl* salt at 312—313°; both compounds are readily hydrolysed by dilute caustic soda. The *chloride* is immediately decomposed by cold water; the *amide* is a white, amorphous powder which melts at 236—237°, and dissolves in water and alcohol. S. B. A. A.

Thioxanthone. By C. Graebe and O. Schultess (*Annalen*, **263**, 1—15).—It has been shown by Ziegler (Abstr., 1890, 1292) that thioxanthone can be obtained from phenylthiosalicylic acid just as xanthone can be prepared from phenylsalicylic acid; the following paper gives a more complete account of the experiments on this subject.

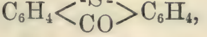
The *diazo*-compound, $COOH\cdot C_6H_4\cdot N_2\cdot SPh$, is precipitated on gradually adding a solution of orthodiazobenzoic acid chloride to a well-cooled dilute solution of sodium thiophenate; it is a yellow, amorphous compound, melts at 60° with explosion, and dissolves unchanged in cold dilute soda or sodium carbonate.

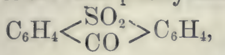
Phenylthiosalicylic acid (*diphenylsulphideorthocarboxylic acid*),

$$SPh\cdot C_6H_4\cdot COOH,$$

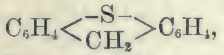
is obtained when the preceding compound is warmed with soda; it separates from dilute alcohol in colourless plates, from glacial acetic acid in needles, melts at 166°, and sublimes readily. It is almost insoluble in cold water, but readily soluble in alcohol, benzene, and glacial acetic acid; it dissolves in warm concentrated sulphuric acid, being thereby converted into thioxanthone, yielding a solution which shows a green fluorescence; phosphorus pentachloride also converts it into thioxanthone. The *potassium* salt, $C_{13}H_9SO_2K$, crystallises in colourless needles, and is readily soluble in water, but only sparingly in alcohol; the *ammonium* salt, $C_{13}H_9SO_2NH_4$, crystallises in colourless needles, and is rather more sparingly soluble than the potassium salt. The *silver* salt is insoluble in water. The *ethyl* salt, $C_{15}H_{14}SO_2$, prepared from the silver salt, crystallises from hot light petroleum in colourless needles, and melts at 151°.

Sulphobenzidorthocarboxylic acid, $SO_2Ph\cdot C_6H_4\cdot COOH$, is formed when the preceding compound is warmed with moderately concentrated (1 : 2) nitric acid; it crystallises from alcohol in colourless needles containing 1 mol. H_2O, and melting at 99°; it loses its water at 100—105°, the anhydrous substance melting at 152°. It is very readily soluble in chloroform, and dissolves freely in alcohol and ether.

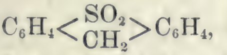
Thioxanthone,  $C_6H_4\left<\begin{matrix}-S-\\CO\end{matrix}\right>C_6H_4$, is obtained when phenylthiosalicylic acid is heated at 100° with concentrated sulphuric acid; it crystallises from chloroform in long, yellow needles, melts at 209°, sublimes readily, and is insoluble in alkalis. When heated with potash at 230°, it is reconverted into phenylthiosalicylic acid.



Benzophenonesulphone, $C_6H_4<\substack{SO_2\\CO}>C_6H_4$, is easily prepared by oxidising thioxanthone with chromic acid in glacial acetic acid solution; it crystallises from alcohol or chloroform in yellowish needles, melts at 185°, and is readily soluble in ether, but only very sparingly in boiling water. It is identical with the compound obtained by Beckmann by heating benzophenone with fuming sulphuric acid. When warmed with zinc-dust and dilute soda, it gives first a violet and then a blue solution, but the colour disappears on exposing the filtered solution to the air, and also if the treatment with zinc-dust is continued for some time; with alcoholic potash it gives the same blue coloration.



Diphenylenemethane sulphide, $C_6H_4<\substack{-S-\\CH_2}>C_6H_4$, prepared by reducing thioxanthone with hydriodic acid and amorphous phosphorus, or by passing orthophenyltolyl sulphide through a red-hot tube, crystallises from chloroform in large needles or prisms, melts at 128°, boils at 340° (730 mm.), and sublimes very readily; it is only sparingly soluble in cold alcohol and ether, but very readily in chloroform, and it dissolves in warm concentrated sulphuric acid with a yellow or yellowish-red coloration, the solution showing a yellow fluorescence; it is readily converted into benzophenonesulphone by oxidising agents.



Diphenylenemethanesulphone, $C_6H_4<\substack{SO_2\\CH_2}>C_6H_4$, is obtained when benzophenonesulphone is reduced with hydriodic acid and amorphous phosphorus; it crystallises from alcohol in colourless needles, melts at 170°, and is readily soluble in hot alcohol and ether.

F. S. K.

Isopropylphenylglycollic Acid and its Derivatives. By M. Fileti and G. Amoretti (*Gazzetta*, **21**, 41—52).—Isopropylphenylglycollic acid, $C_6H_4Pr^{\beta}\cdot CH(OH)\cdot COOH$, has been described by Raab (Abstr., 1876, 398), and by Plöschl (Abstr., 1882, 515). The *magnesium* salt, $(C_{11}H_{13}O_3)_2Mg + 4H_2O$, is a crystalline powder very sparingly soluble in water; the *calcium* salt, $(C_{11}H_{13}O_3)_2Ca + 1\frac{1}{2}H_2O$, crystallises in plates which become anhydrous at 150°; it is also very sparingly soluble in water. The *methyl* salt, $C_{12}H_{16}O_3$, crystallises from light petroleum in needles, melts at 80°, and dissolves in most ordinary solvents, but not in water. The *ethyl* salt, $C_{13}H_{18}O_3$, melts at 40—41° and is very freely soluble in all solvents except water. The *amide* crystallises from benzene in needles, melts at 116°, dissolves readily in alcohol, ether, chloroform, &c., but only sparingly in water. On treating the acid with phosphorus pentachloride, an unstable chloride is obtained which is decomposed by cold water and converted into phenylisopropylchloracetic acid.

Isopropylphenylmethylglycollic acid, $C_6H_4Pr^{\beta}\cdot CH(OMe)\cdot COOH$, prepared by the action of sodium methoxide on isopropylphenylchloracetic acid, crystallises in plates and melts at 52—53°. The *sodium* salt crystallises in brilliant plates containing 2 mols. H_2O, and is very soluble in hot water. *Isopropylphenylethylglycollic acid*,

$$C_6H_4Pr^{\beta}\cdot CH(OEt)\cdot COOH,$$

prepared in the same way as the preceding compound, is a viscous, uncrystallisable liquid. *Isopropylphenylacetylglycollic acid*, $C_6H_4Pr^{\beta}\cdot CH(OAc)\cdot COOH + H_2O$, crystallises from light petroleum in large prisms, and melts at 60—61°; it becomes anhydrous in a vacuum or when heated to near its melting point. It dissolves in the ordinary solvents. It is hydrolysed by boiling with water or dilute sodium carbonate. *Isopropylphenylchloracetic acid*, $C_6H_4Pr^{\beta}\cdot CHCl\cdot COOH$, (Abstr., 1886, 769), prepared by heating isopropylphenylglycollic acid with fuming hydrochloric acid, crystallises from light petroleum in oblique, lamellar prisms and melts at 82°. It is decomposed by water and by alcohol containing traces of water on heating, and by alkaline hydrates and carbonates at the ordinary temperature. The aqueous solution has a strong and persistent sweetish taste. *Isopropylphenylbromacetic acid*, $C_6H_4Pr^{\beta}\cdot CHBr\cdot COOH$, resembles the chlorinated derivative. It crystallises in plates melting at 94—95°. *Isopropylphenylanilidoacetic acid*, $C_6H_4Pr^{\beta}\cdot CH(NHPh)\cdot COOH$, prepared by treating the chlorinated acid with an excess of aniline, forms a crystalline powder, melts at 145—146° with partial decomposition, and dissolves in alcohol and benzene, but not in water, &c. It is not attacked by dilute alkalis.

Isopropylbenzoylformic acid, $C_6H_4Pr^{\beta}\cdot CO\cdot COOH$, prepared by oxidising isopropylphenylglycollic acid with potassium permanganate, crystallises from light petroleum in colourless, rhomboidal plates, melts at 106—107°, dissolves in alcohol and ether and sparingly in water. It is tinged yellow by exposure to light. The *calcium* salt, $(C_{11}H_{11}O_3)_2Ca + 2H_2O$, forms acicular prisms very soluble in water. The *barium*, *zinc*, and *magnesium* salts are equally soluble; the last crystallises in needles. The *ethyl* salt is a liquid with a pleasant odour. The *amide*, $C_{11}H_{13}O_2N$, is obtained as a crystalline powder melting at 189° and soluble in alcohol and chloroform.

Isopropylphenylisonitrosoacetic acid, $C_6H_4Pr^{\beta}\cdot C(N\cdot OH)\cdot COOH$, prepared by treating sodium isopropylbenzoylformate with hydroxylamine, crystallises from its ethereal solution in colourless, lamellar prisms, melts with decomposition at 124°, and dissolves in water, alcohol, and ether. S. B. A. A.

Synthesis of Hydroxyxanthones. By S. v. KOSTANECKI and B. NESSLER (*Ber.*, **24**, 1894—1897).—Orsellenic acid and paraorsellenic acid both yield the same hydroxymethylxanthone, and this is identical with the salicylresorcinol ether described by Michael (Abstr., 1884, 311). When orcinol is distilled with salicylic acid, besides the above-mentioned hydroxymethylxanthone, which the authors denominate the α-derivative, an isomeride, *β-hydroxymethylxanthone*, is simultaneously formed; this crystallises from dilute alcohol in colourless needles and melts at 285°. The two hydroxymethylxanthones have the constitutions $C_6H_4<\genfrac{}{}{0pt}{}{O-}{CO}>C_6H_2Me\cdot OH$ [O : OH : Me = 1 : 3 : 5 and

1 : 5 : 3], although which represents the α- and which the β-compound cannot at present be decided. The β-compound appears also to be formed when the orsellenic acids are distilled with salicylic acid. When resorcinol is distilled with salicylic acid and acetic anhydride, the hydroxyxanthone described by Michael (*loc. cit.*) is obtained as chief product, whilst an *isomeride* which melts at a high temperature, and was not obtained thoroughly pure, is also formed. As Michael's hydroxyxanthone is obtained from resorcinolcarboxylic acid [$(OH)_2 : COOH = 1 : 3 : 4$], it must have the constitution [OH = 3].

1 : 3-*Isoeuxanthone*, $C_{13}H_6O_2(OH)_2$, is formed, together with other products which were not purified, from phloroglucinol and salicylic acid; it is separated from the other compounds by treating the crude product with alkali, and on acidifying the alkaline extract, it is precipitated. It crystallises from dilute alcohol in yellowish needles, and melts at 247°. Experiments are in progress on the action of other phenolic compounds on salicylic acid. A. R. L.

The Tannic Acid of Oak-wood. By C. Böttinger (*Annalen*, **263**, 108—125).—When the acetyl derivative of oak-wood tannic acid is reduced with sodium amalgam in boiling, dilute alkaline solution, it yields a compound of the composition $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6$ (*hydroquercic acid*), a compound of the composition $C_5H_6O_2$ (*querlactone*), an acid, which is in all probability trihydroxybutyric acid, traces of gallic acid, oxalic acid, acetic acid, and oak-wood tannic acid, and a substance of unknown composition, which very readily undergoes oxidation. On acidifying the solution with sulphuric acid, the hydroquercic acid is obtained as a dirty-brown precipitate; the solution is then repeatedly extracted with ethyl acetate, the extract evaporated, and the residue mixed with water. The portion insoluble in water is dissolved in a little alcohol, and the solution treated with a large volume of ether, when hydroquercic acid and another compound, which is readily soluble in acetic anhydride, are precipitated; the filtered solution is evaporated, the residue dissolved in ether, with the addition of a few drops of light petroleum, and the filtrate evaporated. The residual querlactone is separated from a trace of gallic acid by treating with a little water, and is then freed from the readily oxidisable substance referred to above by dissolving it in ether and shaking the solution with ammonia; the oxidisable substance remains in the ethereal solution in combination with some of the querlactone, and on acidifying the ammoniacal solution, the rest of the lactone is liberated as an oil and can be extracted with ether.

Hydroquercic acid, purified by washing with ether, water, and ethyl acetate consecutively, and then dried for two hours in a desiccator, has the composition $C_{15}H_{18}O_7$, but when completely dried in a desiccator, it has the composition $C_{15}H_{16}O_6$; it is precipitated from its solution in acetic acid on the addition of water in a dirty-brown, flocculent condition, has a bitter taste, and is only sparingly soluble in cold water, but moderately easily in boiling water, and readily in alcohol. It dissolves in 20 per cent. nitric acid with evolution of carbonic anhydride, yielding a reddish-yellow solution, and it dissolves slowly in cold concentrated sulphuric acid with a reddish-brown coloration; in its aqueous or acetic acid solution, bromine produces an intensely yellow precipitate. When heated with 20 per cent. hydrochloric acid at 150°, it gives off carbonic anhydride and methyl chloride yielding a dark substance which dissolves only slowly in alkalis; hydriodic acid at 220—225° decomposes it with liberation of carbonic anhydride and methyl iodide, and formation of iodoform and other products. It is hygroscopic, and when heated at 100°, it loses water, which it absorbs again on cooling; heated at 170°, it is converted into a substance which is insoluble in alcohol and dilute acetic acid. The *acetyl* derivative, $C_{15}H_{14}O_6Ac_2$, is a dirty-brown powder. In neutral solutions of the ammonium salt, barium chloride produces a voluminous, amorphous precipitate, which, when dried at 100°, has the composition $(C_{15}H_{15}O_6)_2Ba$; the *lead* salt has the composition $(C_{15}H_{15}O_6)_2Pb$. In neutral solutions of the acid, silver nitrate gives a reddish-brown coloration, and on adding acetic acid to the solution, an acid silver salt is precipitated.

Querlactone, $C_5H_6O_2$, melts at a low temperature and separates from water as an oil; it is very readily soluble in acetic acid, alcohol, ether, and ethyl acetate, but insoluble in benzene and light petroleum. When boiled with barium hydroxide, it is converted into a barium salt which is insoluble in water, but soluble in acetic acid. It reduces ammoniacal silver nitrate in the cold, and is only very slowly decomposed by 20 per cent. hydrochloric acid at 150°; the *lead* salt has the composition $(C_5H_7O_3)_2Pb$. A compound analogous to querlactone can also be obtained from the acetyl derivatives of oak-bark and pine-bark tannic acids.

The oxidisable substance mentioned above dissolves freely in ether and alcohol, but is only sparingly soluble in benzene and light petroleum; when its ethereal solution is filtered through paper, the latter is coloured intensely red. When the freshly prepared substance is agitated with a drop of concentrated ammonia in the dark, it yields a colourless, seemingly crystalline mass which immediately turns red on exposure to light; it loses this property on keeping. The freshly prepared substance gives an intense rose-red coloration on boiling with silver nitrate, ferric chloride, or copper sulphate, but when it has been kept for some time, it reduces silver nitrate in the cold, and ferric chloride on boiling, without any coloration being produced.

When the acetyl derivative of oak-bark tannic acid is reduced with sodium amalgam as described above, it yields hydroquercic acid, hydroquergalic acid, lagic acid, $C_4H_4O_3$, identical with the compound obtained by the oxidation of gallic acid, trihydroxybutyric acid, a little gallic acid, and other compounds; the hydroquergalic acid can be separated from the hydroquercic acid by treating the mixture of the two compounds with 20 per cent. acetic acid, in which the latter is the more readily soluble.

Hydroquergalic acid is a brownish-red, amorphous compound, readily soluble in boiling water, but only sparingly in cold water and insoluble in boiling alcohol, ether, ethyl acetate, acetic anhydride, and acetic acid; in neutral solutions of the ammonium salt, many metallic salts produce brown, amorphous precipitates. The acid, dried over sulphuric acid, has the composition $C_{14}H_{14}O_6$, and loses approximately 1 mol. H_2O at 100°; when heated with alcoholic potash and ethyl iodide, it is partially converted into an ethyl salt, which is readily soluble in alcohol, ethyl acetate, and acetic acid.

F. S. K.

Some Derivatives of Phthalic Sulphinide. By C. W. Moulton (*Amer. Chem. J.*, **13**, 193—203).—Phthalic sulphinide (Abstr., 1885, 539) is best prepared as follows:—Finely powdered naphthalene (1 kilo.) is rubbed up with sulphuric acid (750 grams) in the cold; it is then heated on the water-bath until the naphthalene melts, and kept at this temperature with constant stirring for two hours; the whole is poured into 12 litres of water at 85°, cooled to 50°, filtered through cloth, neutralised with chalk, again filtered, and precipitated with sodium carbonate. It is once more filtered and evaporated to 2 litres, when sodium α-naphthalenesulphonate crystallises on cooling; this is filtered, dried (finally at 185°), powdered, and treated with 80 per cent. of its weight of phosphoric chloride; after driving off the oxychloride on the water-bath, the mass is cooled and washed once with cold water. The chloride is added by degrees to an excess of strong ammonia, kept cool; the excess of ammonia is expelled on the water-bath, and the sulphonamide (450 grams) washed by boiling in 2 or 3 litres of water, cooled, filtered, and dried. To oxidise the sulphonamide, potassium hydroxide (180 grams) and potassium permanganate (900 grams) are dissolved in 12 litres of water at 40° and 200 grams of the amide stirred in; the mixture is kept at 60—100° until the permanganate is reduced; after filtering and washing the manganese dioxide by boiling it in water, hydrochloric acid is added to the mixed filtrate and washings, until they are nearly neutral; the whole is evaporated to 1 litre, and excess of hydrochloric acid added, when the acid potassium salt of the sulphinide crystallises; it is recrystallised from water and boiled (25 grams) with water (450 c.c.) and hydrochloric acid (50 c.c. of sp. gr. 1·175) for 15 minutes and slowly evaporated to obtain the phthalic sulphinide. The yield of the acid potassium salt is 40—45 grams.

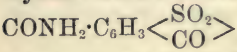
When phthalic sulphinide is heated for some time with hydrochloric acid, it is converted into acid ammonium sulphophthalate. (Compare Remsen and Burton, Abstr., 1890, 94.)

When phthalic sulphinide is dissolved in an alcohol and the solution saturated with hydrogen chloride and boiled, the corresponding alkyl salt of sulphaminephthalic acid is obtained.

Dimethyl α-sulphaminephthalate, $SO_2NH_2\cdot C_6H_3(COOMe)_2$, crystallises in long, narrow, very thin plates, which have a characteristic nacreous lustre when dried on the filter; it melts at 135° and dissolves in hot water.

Diethyl α-sulphaminephthalate forms long, needle-shaped crystals arranged in bundles; it melts at 101·5—102°, and is less soluble in water and less stable than the dimethyl derivative.

Dipropyl α-sulphaminephthalate is difficult to crystallise; those crystals which were obtained, melted between 64° and 68°, the latter temperature being more probably correct.

Crystals of $SO_2NH_2\cdot C_6H_3(CONH_2)_2$ were obtained when the diethyl salt was treated with excess of ammonia in the cold for 24 hours, and then heated and concentrated on the water-bath. When these crystals were dissolved in water and acidified, *carbamine sulphinide*,  $CONH_2\cdot C_6H_3<^{SO_2}_{CO}>NH$, was precipitated; this compound forms tabular crystals, melts at 275° (uncorr.), and dissolves in water somewhat sparingly, and in boiling alcohol slightly, but not in ether; the *ammonium*, *barium*, and *silver* salts are described.

α-Sulphophthalic acid was prepared by converting the acid ammonium salt, obtained from phthalic sulphinide (see above), into chloride by phosphoric chloride, and boiling this with water; it is very soluble in water and in absolute alcohol, but not in ether; it is difficult to crystallise; some crystals which were obtained melted at 62—64°. Attempts to obtain an anhydride of sulphophthalic acid failed. A. G. B.

Symmetrical Alkylisophthalic Acids. By O. DOEBNER (*Ber.*, **24**, 1746—1753).—Attempts to isolate the intermediate product of the reaction between pyruvic acid and an aldehyde in the presence of barium hydroxide have led to negative results; its formation is, however, indicated by the fact that a purer ultimate product is obtained when the mixture is boiled for a longer period than that previously given (Abstr., 1890, 1283). Ethylisophthalic acid is prepared by boiling together a mixture of pyruvic acid (50 grams), propaldehyde (16 grams), and barium hydroxide (120 grams) dissolved in water (1 litre) for 15—20 hours in a reflux apparatus; it is isolated as already described (*loc. cit.*), and is best purified by crystallisation from a mixture of acetone and water (equal parts); it melts at 263°. The *barium salt* separates from concentrated aqueous solutions in needle-shaped crystals containing 5 mols. H_2O; it loses $3\frac{1}{2}$ mols. H_2O at 140°, but the remainder is not expelled by heating at 200°; whilst the *calcium salt* forms prismatic crystals containing 3 mols. H_2O, and is easily soluble in water.

Isopropylisophthalic acid is produced from pyruvic acid (50 grams) and isobutaldehyde (20 grams); the yield is 10 grams, or about double that previously obtained. It is best purified by repeated crystallisation from dilute acetone, and then melts at 285°. The *barium salt* forms small, hygroscopic, prismatic crystals which contain $2\frac{1}{2}$ mols. H_2O, and retain $\frac{1}{2}$ mol. H_2O when heated at 200°; the *calcium salt* forms small crystals containing $2\frac{1}{2}$ mols. H_2O, easily soluble in water; the *silver salt* is a white powder containing 1 mol. H_2O, insoluble in water; whilst the *lead*, *copper*, and *mercury salts* are amorphous precipitates sparingly soluble in water. Isopropylbenzene and carbonic anhydride are obtained when the calcium and other salts are heated.

Isobutylisophthalic acid is prepared from pyruvic acid (50 grams) and isovaleraldehyde (25 grams); the yield of pure acid is 8 grams. It separates from dilute acetone in small, colourless plates, and melts at 269°. The *barium salt* forms hygroscopic, prismatic crystals containing 3 mols. H_2O, and is easily soluble in water; it loses $2\frac{1}{2}$ mols.

H_2O at 140°. The *calcium salt* crystallises from a small quantity of water with 2 mols. H_2O; whilst the *silver* salt is a white, anhydrous precipitate, sparingly soluble in water.

Phenylisophthalic acid is obtained by boiling pyruvic acid (50 grams) and benzaldehyde (30 grams) with the above-mentioned quantity of barium hydroxide solution for 15 hours. As the barium salt is sparingly soluble in hot water, the chief portion occurs in admixture with the precipitate of barium oxalate and carbonate; the yield of pure acid is 8 grams. The *barium salt* crystallises in small needles containing $4\frac{1}{2}$ mols. H_2O; it loses $3\frac{1}{2}$ mols. H_2O at 140°; the *calcium salt* forms small, anhydrous crystals, and is sparingly soluble in water; whilst the copper salt is a bluish-green, and the *silver* and *lead* salts are white precipitates which are sparingly soluble in water. Phenylisophthalic acid is the only known dicarboxyl-derivative of diphenyl which contains both the carboxyl groups in one nucleus.

Furfurisophthalic acid, $C_4OH_3{\cdot}C_6H_3(COOH)_2$, is produced by the action of barium hydroxide solution on a mixture of pyruvic acid (50 grams) and furfuraldehyde (28 grams); the yield is only 1 gram; it crystallises from dilute acetone in dense, glistening needles, melts at 290° with decomposition, and is sparingly soluble in water, readily in alcohol, ether, acetone, and benzene. The *barium salt* is soluble in hot water; whilst the lead, silver, and copper salts are sparingly soluble precipitates. A. R. L.

Stereo-isomeric Methylphenylsuccinic Acids. By N. ZELINSKY and L. BUCHSTAB (*Ber.*, **24**, 1876—1880).—*Ethyl α-bromophenylacetate* boils at 150—151° under a pressure of 10—15 mm.

Ethyl methylphenylcyanosuccinate, $COOEt{\cdot}CMe(CN){\cdot}CHPh{\cdot}COOEt$, is prepared by dissolving ethyl α-cyanopropionate (b. p. 195—200°) and sodium in equivalent proportion in alcohol, and gradually adding ethyl α-bromophenylacetate (1 mol.). Much heat is developed, causing the mixture to boil; the reaction is completed by heating on the water-bath for 2—3 hours, water is then added, and the heavy oil which separates extracted with ether. On distilling the ethereal solution, the compound is obtained as an oil boiling at 320—330°. When heated with aqueous potash, and the alkaline liquid washed with ether, acidified with hydrochloric acid, and then extracted with ether, an oily product, probably a tricarboxylic acid, is obtained; when the latter is dissolved in concentrated sulphuric acid, water added to incipient turbidity, and the mixture boiled for some time, *methylphenylsuccinic acid* separates in crystals.

Methylphenylsuccinic acid may be separated into two isomerides by fractional crystallisation from water; the less soluble modification, which is formed in the larger quantity, melts at 192—193°, at the same time losing water and forming the anhydride, whilst the more soluble modification melts at 170—171°.

When methylphenylsuccinic acid (m. p. 192—193°) is slowly brought to a temperature of 120—130°, water is eliminated, and on quickly raising the temperature to 310—320° the anhydride passes over as an oil. When the latter is boiled with water, it dissolves and methylphenylsuccinic acid (m. p. 192—193°) separates on cooling, whilst the acid (m. p. 170—171°) is obtained from the filtrate. On the other hand, the acid (m. p. 170—171°) is exclusively formed when the anhydride is exposed to the air. The electrical conductivities are as follows:—

Methylphenylsuccinic acid (m. p. 170—171°) k 0·0233.
,, ,, (m. p. 192—193°) k 0·0372.

The strongly negative character of the phenyl group is exemplified in the much higher values obtained in the case of the above-described acids, compared with those obtained with the two dimethylsuccinic acids (*Zeit. physikal. Chem.*, **5**, 405). The question whether the anhydride exists in two stereo-isomeric modifications is still open.

A. R. L.

Action of Urea on Sulphanilic Acid. By J. VILLE (*Compt. rend.*, **112**, 868—870).—An intimate mixture of finely-powdered urea (1·5 mols.) and sulphanilic acid (1 mol.) becomes pasty at 105°, begins to melt at about 110°, but becomes solid again at 115—120°. If heated for three or four hours at 125°, ammonia is evolved; the product, after cooling, is dissolved in water, mixed with barium hydroxide, and allowed to remain in a vacuum over sulphuric acid for 48 hours, in order to decompose the ammonium salt that has been formed. Excess of barium is removed by means of carbonic anhydride, and the concentrated filtrate, when mixed with alcohol, yields a precipitate of the barium salt which can be purified by repeated solution in water and precipitation by alcohol, and from which the acid is obtained by treatment with the calculated quantity of sulphuric acid. The filtered liquid is evaporated on a water-bath, and afterwards in a dry vacuum, when *sulphanilocarbamic acid*, $C_7H_8N_2SO_4$, separates in feathery, microscopic lamellæ, very soluble in water, somewhat easily soluble in acids, but quite insoluble in ether, chloroform, and benzene. It is strongly acid, decomposes carbonates, and forms crystallisable salts. The barium salt crystallises with 3 mols. H_2O in monoclinic prisms, soluble in water, but insoluble in alcohol; it becomes anhydrous at 95°, and then has the composition

$$Ba(C_7H_7N_2SO_4)_2.$$

When the acid is heated in sealed tubes at 100° with excess of barium hydroxide solution, it yields ammonia, carbonic anhydride, and sulphanilic acid in equal molecular proportions. This decomposition and its mode of formation show that the acid has the constitution $SO_3H{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$.

C. H. B.

Nitrocymenesulphonic Acids. By G. ERRERA (*Gazzetta*, **21**, 65—76).—*Nitro-α-cymenesulphonic acid* (compare Abstr., 1890, 1287), when perfectly pure, crystallises in pale-yellow needles free from any reddish tinge, and its aqueous solution is not reddened by light. The pure *barium* salt crystallises in slender, silky, yellow needles containing 1 mol. H_2O; the pure *magnesium* salt crystallises in bright-yellow tables containing 5 mols. H_2O; the *lead* salt in bright-yellow needles containing 1 mol. H_2O; the *zinc* salt in large, pale-yellow, rhombic tables containing 6 mols. H_2O, and the *calcium* salt in yellow plates with 1 mol. H_2O.

The *lead* salt of amido-α-cymenesulphonic acid crystallises in red nodules with 4 mols. H_2O. On diazotising this acid, *diazo-α-cymenesulphonic acid* is formed, and separates in very slender needles. It is decomposed by treatment with absolute alcohol with the formation of Widman's ethoxy-α-cymenesulphonic acid. The *barium* salt of this acid is soluble in water, and crystallises in silvery plates containing 3½ mols. H_2O. The *barium* salt of chloro-α-cymenesulphonic acid (Abstr., 1890, 1287) crystallises in colourless, lustrous plates containing 3 mols. H_2O.

The authors previously isolated (*loc. cit.*) from the mother liquors obtained in the preparation of barium nitrocymenesulphonate an abnormal magnesium salt crystallising with 6 mols. H_2O, but otherwise identical in composition with the normal salt. The *barium* salt corresponding to this modification crystallises with 5 mols. H_2O; the *lead* salt, $(NO_2 \cdot C_6H_2PrMe \cdot SO_3)_2Pb,5H_2O$, crystallises in small, pale, yellowish needles; the *zinc* salt forms small needles containing 6 mols. H_2O; and the *calcium* salt almost colourless needles with 9 mols. H_2O. These salts cannot be converted into the corresponding normal nitrocymenesulphonates, with which they are probably isomeric. The acids derived from both series of salts, however, seem to yield the same amido-derivative. S. B. A. A.

Unsaturated Sulphones. By R. OTTO (*Ber.*, **24**, 1510).—Unsaturated sulphones are readily obtained by the action of sodium benzenesulphinate or paratolylsulphinate on allyl chloride. *Phenylallylsulphone* is an oil, but *paratolylallylsulphone* crystallises in splendid monosymmetric prisms or tablets, and melts at 52—53°. Both compounds readily combine with bromine, forming additive compounds.

H. G. C.

Certain Sulphone Derivatives and their Hydrolysis in Alkaline Solution. By W. AUTENRIETH (*Ber.*, **24**, 1512—1519).—In continuation of the work done by Stuffer (this vol., p. 180) and by himself (this vol., p. 567), the author has prepared some new sulphone derivatives and examined their behaviour towards alkalis, and has also been able to confirm the statement of Stuffer that in hydrolysing ethylsulphonesulphonal all the sulphone groups are eliminated as ethylsulphinic acid, no methylphenylsulphone being formed.

Ethylsulphonephenylsulphonal, $CMe(SO_2Ph)_2 \cdot CH_2 \cdot SO_2Et$, is obtained by carefully oxidising the phenylmercaptole of thioethylacetone (this vol., p. 567), and crystallises from alcohol or ether in small, lustrous needles, melts at 138—139°, is sparingly soluble in boiling water and in cold alcohol and ether, readily in chloroform. It is readily hydrolysed by decinormal potash solution, 2 mols. of benzenesulphinic acid and 1 mol. of ethylsulphinic acid being formed.

In the author's previous paper, the preparation of the phenylmercaptole of thiophenylacetone was described. A much better yield of this compound is obtained by passing a slow current of hydrogen chloride into an ice-cold mixture of thiophenylacetone and phenylmercaptan, pouring the product after some hours into water, and recrystallising the precipitated compound from alcohol. No reaction takes place between this compound and potassium permanganate in aqueous solution, but on addition of benzene, oxidation slowly takes place, *αβ-diphenylsulphone-β-thiophenylpropane*,

$$SPh\cdot CMe(SO_2Ph)\cdot CH_2\cdot SO_2Ph,$$

being formed. The latter crystallises from alcohol in slender needles, melts at 156—157°, and is sparingly soluble in ether and cold alcohol, readily in chloroform. On treatment with potash, it yields methylphenylsulphone, phenylmercaptan, and benzenesulphinic acid. All attempts to convert the remaining thiophenyl group into a sulphone group were without success. The compound is also probably identical with that obtained by Otto and Rössing by the oxidation of phenylsulphoneacetonemercaptole (this vol., p. 568).

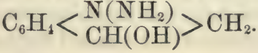
From the results described in this and in previous papers, it appears that whilst the sulphones of the general formula $CR_2(SO_2R)_2$ are stable towards alkalis, the addition of the groups SO_2Ph, SO_2Et, or of chlorine, has such an effect on the molecule that all three sulphone groups are eliminated by an alkali in the form of a sulphinic acid. Further, disulphonesulphides of the formula

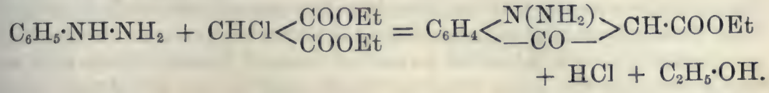
$$CR(SO_2R)(SR)\cdot CH_2\cdot SO_2R$$

behave towards alkalis in a similar manner to alkylene sulphones with adjacent sulphone groups, only one of these being eliminated as a sulphinic acid. H. G. C.

Action of Phenylhydrazine on Ethyl Chloromalonate. By R. Burmeister and A. Michaelis (*Ber.*, **24**, 1800—1802).—When ethyl chloromalonate (1 mol.) and phenylhydrazine (3 mols.) are mixed together, separation of phenylhydrazine hydrochloride and slow evolution of nitrogen take place. After two days, the former is filtered off, the filtrate extracted repeatedly with ether, and the ethereal solution washed several times with dilute hydrochloric acid. On evaporation, an oil is obtained which quickly solidifies, and after recrystallisation from hot ether forms colourless needles, melts at 90°, and reduces Fehling's solution on boiling. It has the composition $C_{11}H_{14}N_2O_3$, and combines directly with phenyl cyanate and phenylthiocarbimide, forming the crystalline additive compounds $C_{18}H_{19}N_3O_4$ and $C_{18}H_{19}N_3O_3S$. The former crystallises in colourless needles and melts at 158°, whilst the latter forms transparent prisms and melts at 141°.

The original product of the reaction dissolves readily in aqueous or alcoholic potash, and the former solution on addition of hydrochloric acid at once yields a compound crystallising in glistening plates, which, after recrystallising from alcohol, melts at 192°, and has the composition $C_9H_8N_2O_2$. It differs, therefore, from the first compound by containing the elements of alcohol less.

The constitution of these substances is not yet finally settled, but the authors believe they are probably derivatives of an amidodihydroindoxyle,  $C_6H_4<\genfrac{}{}{0pt}{}{N(NH_2)}{CH(OH)}>CH_2$. The compound melting at 90° is probably $C_6H_4<\genfrac{}{}{0pt}{}{N(NH_2)}{CH(OH)}>CH\cdot COOEt$, and is formed in the following manner:—



$$C_6H_5\cdot NH\cdot NH_2 + CHCl<\genfrac{}{}{0pt}{}{COOEt}{COOEt} = C_6H_4<\genfrac{}{}{0pt}{}{N(NH_2)}{—CO—}>CH\cdot COOEt + HCl + C_2H_5\cdot OH.$$

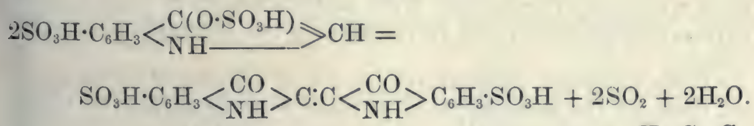
The carbonyl group of this compound is then reduced by the action of the third mol. of phenylhydrazine, nitrogen being simultaneously evolved.

H. G. C.

Synthesis of Indigotindisulphonic Acid (Indigocarmine). By B. Heymann (*Ber.*, **24**, 1476—1478).—It has already been shown by Heumann (this vol., p. 75) that phenylglycocine may be converted into indigotin by fusion with caustic potash and oxidation of the resulting leuco-compound. Other dehydrating agents, such as sulphuric acid and zinc chloride, do not have the same effect. The author finds, however, that if, instead of concentrated sulphuric acid, fuming acid be employed, indigotindisulphonic acid is readily obtained. This may be shown on the small scale by gently warming phenylglycocine with fuming sulphuric acid in a test-tube, a yellow solution being obtained which when poured on to ice shows the characteristic colour of indigocarmine solution.

On the large scale, the following method is adopted:—1 part of phenylglycocine is mixed with 10—20 parts of sand, and 20 times the quantity of sulphuric acid containing 80 per cent. of anhydride gradually added, the temperature not being allowed to rise above 30°. The yellow solution, on addition of ordinary concentrated sulphuric acid, evolves sulphurous anhydride, and assumes the deep blue colour of indigo; ice is then added, and the colouring matter precipitated by addition of common salt. The yield of pure indigocarmine thus obtained is about 60 per cent. of the phenylglycocine employed.

The mechanism of the reaction is not yet clear; possibly the sulphonic acid of indoxyle sulphate is first formed, and on addition of sulphuric acid undergoes the following reaction:—



$$2SO_3H\cdot C_6H_3<\genfrac{}{}{0pt}{}{C(O\cdot SO_3H)}{NH——}>CH = SO_3H\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO}{NH}>C:C<\genfrac{}{}{0pt}{}{CO}{NH}>C_6H_3\cdot SO_3H + 2SO_2 + 2H_2O.$$

H. G. C.

Hydrobenzoïns and their Anhydrides. By K. Auwers (*Ber.*, **24**, 1776—1783).—The author has repeated the experiments of Zincke (Abstr., 1880, 114), in the hope of obtaining again the substances prepared in small quantity by him, as these might possibly be isomerides of benzoïn and benzile. This expectation has, however, not been fulfilled, but a number of other observations have been made in the hydrobenzoïn group, and are given in this paper.

Concentrated nitric acid of sp. gr. 1·4 acts on both hydrobenzoïns at the ordinary temperature or even at 0°, with formation of benzoïn.

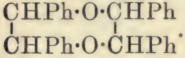
The oxidation takes place more slowly with the iso-compound, and the product is also frequently oily for a short time, but crystallises eventually to a magma of needles. If the mixture be slightly warmed, the oxidation product of isohydrobenzoïn cannot be obtained crystalline. The anhydrides are attacked in a similar manner at the ordinary temperature. A mixture of equal volumes of fuming nitric acid and acetic acid has the same effect as nitric acid alone, but a cold acetic acid solution of potassium dichromate or dilute potassium permanganate solution, like chromic anhydride, converts both compounds into benzaldehyde.

Bromine acts on both hydrobenzoïns in acetic acid solution at 100° with formation of benzile and smaller quantities of stilbene bromide. A somewhat similar reaction has been observed by Pechmann (Abstr., 1890, 1222). Both compounds also unite directly with orthotolyl cyanate on heating at 100° under pressure, yielding additive compounds having the formula $(CHPh\cdot O\cdot CO\cdot NH\cdot C_6H_4Me)_2$. That obtained from hydrobenzoïn crystallises in colourless needles melting at 233—234°, and that from the iso-compound in small needles melting at 163°.

When stilbene bromide is heated with alcoholic potassium hydrosulphide, the oily product obtained is stilbene, and not, as would be expected, bromostilbene or tolane (see also Forst and Zincke, this Journal, 1876, ii, 634).

In the preparation of the anhydrides by Zincke's method, diphenylacetaldehyde, $CHPh_2\cdot CHO$, is always obtained as a bye-product. On treatment with hydroxylamine, it yields *diphenylacetaldoxime*, $CHPh_2\cdot CH{:}NOH$, which forms slender, white needles and melts at 120°. A small quantity of another substance containing nitrogen is also formed in the reaction, but the amount was insufficient to determine whether it was an isomeric oxime.

The molecular weights of the anhydrides as determined by Raoult's method agree with the double formula $C_{28}H_{24}O_2$, and these are, therefore, in all probability ether-like compounds having the constitution



$$\begin{array}{l}CHPh\cdot O\cdot CHPh\\ \mid\qquad\qquad\;\mid\\ CHPh\cdot O\cdot CHPh\end{array}$$

. The hydrobenzoïn anhydride is best prepared by gently warming hydrobenzoïn with half its weight of phosphoric anhydride, adding water, and recrystallising the insoluble portion from alcohol.

In order to obtain comparative molecular weights of other anhydrides, those of the dimethylsuccinic acids were examined by Raoult's method. In both cases the results agreed with the simple formula $C_6H_8O_3$.

H. G. C.

Aldehyde-green. By W. v. Miller and J. Plöchl (*Ber.*, **24**, 1700—1715).—Aldehyde-green was discovered by Cherpin in 1862, and was shown to contain sulphur by Hofmann (*Ber.*, **3**, 761), who ascribed to it a provisional formula. Lucius, however (*Würtz Dict.*, **1**, 234), states that it does not contain sulphur, as it is produced by the action of aldehyde on an acid solution of rosaniline, the function of the sodium thiosulphate subsequently used being merely to precipitate the blue and violet dyes which are formed simultaneously.

Aldehyde-blue, prepared by Gattermann and Weichmann's method (Abstr., 1890, 503), is precipitated from its aqueous solution by sodium chloride, and when the filtrate has a blue colour this is due to the use of too little precipitant and not to the presence of a second blue dye, as stated by Gattermann and Weichmann; the green dye, however, which these chemists obtained from the same filtrate, exists ready formed, and separates, after a time, or more quickly when it is heated; it is probably identical with the non-sulphuretted aldehyde-green (see below). Aldehyde-blue has the composition $C_{31}H_{37}N_3O_3Cl_2$; it is not a quinaldine derivative, as stated by Gattermann and Weichmann (*loc. cit.*), but the hydrochloride of an anhydroaldolpararosaniline, $OH{\cdot}C(C_6H_4{\cdot}N{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}OH)_3$; a similar blue dye is formed from isobutaldehyde and pararosaniline.

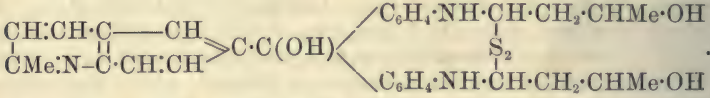
When pararosaniline (50 grams), concentrated hydrochloric acid (200 grams), and paraldehyde (100 grams) are heated together on the water-bath for three hours, a brownish solution is formed; this is diluted to 4 litres, saturated with hydrogen sulphide, and an excess of sulphurous acid added, when a resinous mass, together with sulphur, separates out. It is filtered, and the operation repeated; on adding ammonia to the filtrate, a colourless base separates, which is spread on a porous tile, and then dried at 65° in a current of hydrogen; it is soluble in acids, ether, alcohol, and benzene, and has the composition $C_{31}H_{29}N_3 + \frac{1}{2}H_2O$; the yield is 35—45 grams. The compound is the leuco-base of a green dye, which latter is produced on treating it with lead peroxide in an acid solution, or with chloranil in an alcoholic solution; it has the constitution $C_9NH_5Me{\cdot}CH(C_9NH_7Me)_2$, and thus contains one quinaldine and two dihydroquinaldine residues. When the base is dissolved in dilute hydrochloric acid and treated with nitrous acid, a resinous substance is formed, which is soluble in ether, but does not yield the dye on oxidation. The *monobenzoyl derivative* is prepared by dissolving the base in benzene, gradually adding benzoic chloride, and shaking the mixture with aqueous soda; it is hydrolysed when heated at 120° with concentrated hydrochloric acid. When the base is dissolved in glacial acetic acid, and treated with bromine, a brown, amorphous substance is obtained; this does not yield a dye on oxidation; when, however, it is treated with tin and hydrochloric acid, a base giving a green dye on oxidation is formed, and when boiled with tin and hydrochloric acid, a base giving a blue dye on oxidation is obtained. That the above-described leuco-base is not quite a homogeneous substance, is seen by the following:—When an ethereal solution of it is mixed with one of chloranil, a deep-blue colour is produced, and, later, flocks of a coppery lustre separate, whilst the green dye is obtained from the filtrate by evaporation; the composition of these dyes could not be determined with certainty. When aldehyde-blue is heated at 70° with concentrated hydrochloric acid, and alcohol added, a green coloration is produced; isobutaldehyde-blue gives no such coloration. The directions given by Lucius for the preparation of aldehyde-green are as follows:—Pararosaniline (8 grams) is dissolved in dilute sulphuric acid (20 grams of acid to 30 grams of water), and heated at 50° with aldehyde (40 grams) until a drop of the mixture yields a greenish-blue colour with alcohol.

If instead of treating this solution, diluted to $1\frac{1}{2}$ litres, with hydrogen sulphide and sulphurous anhydride, as Lucius directs, sodium chloride is added, a blue dye is precipitated, and on adding sodium acetate to the filtrate from this, a green dye separates. The latter is air-dried, washed with water, and twice dissolved in alcohol and reprecipitated with ether; it is then shaken with dilute ammonia, collected and washed, and after again dissolving in alcohol and reprecipitating with ether, it is dried in a current of hydrogen at 55°. It has the composition represented by the formula

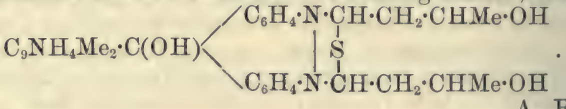
$$C_9NH_5Me\cdot C(OH)(C_6H_4\cdot N\colon CH\cdot CH_2\cdot CHMe\cdot OH)_2,$$

and is the parent compound of ordinary aldehyde-green (see below), which it resembles, but is more fugitive towards light; its production, therefore, explains Lucius' observation that aldehyde-green does not contain sulphur. Aldol reacts with diamidotriphenylmethane, and a leuco-base, $CHPh(C_6H_4\cdot N\colon CH\cdot CH_2\cdot CHMe\cdot OH)_2$, is formed; this, on oxidation, yields a green dye closely resembling that obtained by the preceding method.

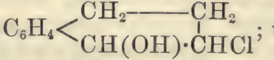
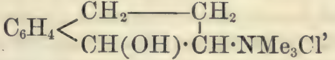
When pararosaniline is dissolved in dilute sulphuric acid and heated with aldehyde (as above) at 50° for three hours, and the product is poured into hydrogen sulphide solution (3 litres) heated to 90°, and sulphurous acid (200 grams) added, the mixture being then boiled for some time, a blue dye separates on adding sodium chloride (300 grams); sodium acetate then precipitates aldehyde-green from the filtrate; the latter has the constitution



When the non-sulphuretted green, prepared from ordinary rosaniline and aldehyde, is boiled with a solution of sodium thiosulphate (Cherpin's method), Usèbe's aldehyde-green is formed, and is isolated in the same manner as the last-described colouring matter; it has the constitution



A. R. L.

A Closed Chain Analogue of Ethylene. By E. Bamberger and W. Lodter (*Ber.*, **24**, 1887—1888).—The authors come to the conclusion that dihydronaphthylene is an analogue of ethylene. It combines with hypochlorous acid forming *tetrahydronaphthylene chlorhydrin*,  $C_6H_4{<}\begin{matrix}CH_2\text{——}CH_2\\ CH(OH)\cdot CHCl\end{matrix}$; this yields a crystalline *ammonium derivative*,  $C_6H_4{<}\begin{matrix}CH_2\text{——}CH_2\\ CH(OH)\cdot CH\cdot NMe_3Cl\end{matrix}$, corresponding with choline hydrochloride.

When tetrahydronaphthylene chlorhydrin is treated with alkalis, three *isomerides* of the formula $C_{10}H_{10}O$, a *dihydric alcohol*, $C_{10}H_{12}O_2$, and naphthalene are formed according to the conditions of the experiment. The initial product, *tetrahydronaphthylene oxide*, $C_{10}H_{10}\colon O$, is a crystalline, comparatively easily volatile compound, and is of especial interest as the first representative of closed ring oxides. The strain which prevails within the molecule, and thereby the tendency to disrupt the union by means of oxygen of the two carbon atoms, causes it to combine with other radicles; thus, when added to a solution of ferric chloride, a precipitate of ferric oxide is produced, whilst the compound unites with the elements of hydrogen chloride. Further details will be given later. A. R. L.

Decomposition of some Diazo-compounds of Naphthalene with Alcohol. By W. R. ORNDORFF and F. L. KORTRIGHT (*Amer. Chem. J.*, **13**, 153—164).—*α-Diazonaphthalene sulphate* was prepared by mixing α-naphthylamine (10 grams) with water and sulphuric acid (40 grams), and passing nitrous fumes into the cooled mixture as long as they were absorbed; the liquid was filtered quickly, alcohol and ether added, and the mixture cooled in ice and salt until the sulphate crystallised. The yield was 79 per cent. of the theoretical. The sulphate crystallises in light-yellow, flat needles, and explodes feebly at 115°; it dissolves easily in water, slightly in alcohol, and not at all in ether; it becomes green on exposure to light. When it was heated at 70—75° with alcohol, nitrogen was evolved, together with some aldehyde; by subsequently distilling off the alcohol, then distilling the residue with steam, and further treating this distillate, naphthalene (40 per cent. of the diazonaphthalene sulphate taken) and α-ethoxynaphthalene (b. p. 277° at 748 mm.; sp. gr. 1·0746 at 0°/4°; 23 per cent. of the sulphate taken) were obtained. The identity of the latter compound was confirmed by preparing it from α-naphthol, after Henriques' method (*Annalen*, **244**, 72). When α-diazonaphthalene sulphate is heated with water at 80—90°, nitrogen is evolved, whilst a colouring matter, some tar, and α-naphthol are formed.

β-Diazonaphthalene sulphate is prepared similarly to the α-salt, but a large excess of sulphuric acid is necessary; the yield is 74 per cent. of the theoretical. It forms flat, needle-shaped, yellow, biaxial crystals, which can be obtained nearly white by recrystallisation, but become green, and finally brown on exposure to light; it explodes feebly at 115°. When decomposed by alcohol, it yields about 30 per cent. in the form of β-ethoxynaphthalene and 7 per cent. in the form of naphthalene, a small quantity of β-naphthol being formed at the same time. When it is heated with water, the same reaction takes place as in the case of the α-salt. The action of hydrochloric acid (40 per cent.) on β-diazonaphthalene sulphate at the ordinary temperature converts about 50 per cent. of the salt into β-chloronaphthalene, a considerable quantity of β-naphthol being also formed.

β-Diazonaphthalene nitrate, obtained (53 per cent. of theoretical yield) by diazotising a well-cooled mixture of β-naphthylamine (10 grams), water, and nitric acid of sp. gr. 1·426 (10 grams), crystallises in flat, yellow needles, from a mixture of water, alcohol, and ether; it dissolves in water, but not in absolute alcohol or ether; it becomes red in light, and explodes at 100° or by percussion. When decomposed by alcohol, about 26 per cent. of it is converted into β-ethoxynaphthalene, and 7 per cent. into naphthalene, a small quantity of nitro- and dinitro-naphthol being formed at the same time.

β-Ethoxynaphthalene melts at 37°, not 33° (Schaeffer, *Annalen*, **152**, 287).

The above results indicate that with the diazonaphthalene compounds, when the diazo-group is in the α-position, the tendency is towards the introduction of hydrogen, resulting in the formation of naphthalene, when they are decomposed by alcohol; but when the diazo-group is in the β-position, the tendency is towards the introduction of the ethoxy-group, in place of the diazo-group, resulting in the formation of an ethoxynaphthalene (compare Remsen and others, Abstr., 1888, 268; 1889, 975). A. G. B.

Orthoazo-compounds of α-Naphthol (β-Naphthaquinone Hydrazones). By E. NOELTING and E. GRANDMOUGIN (*Ber.*, **24**, 1597—1600).—These compounds were prepared to compare their colours with those of the compounds of the para-series.

Parasulphophenylazo-α-naphthol, $OH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$ [$OH : N_2 = 1 : 2$; $SO_3H : N_2 = 1 : 4$], is obtained by shaking β-naphthaquinone (1 mol.) suspended in acetic acid with a cold concentrated aqueous solution of sodium paraphenylhydrazinesulphonate (1 mol.). A red precipitate of the sodium salt is obtained. The *sodium* salt is sparingly soluble in alcohol and cold water, easily in boiling water, and crystallises in beautiful red prisms. The free acid is obtained by adding hydrochloric acid to a solution of the sodium salt. In an acid bath, the azo-compound dyes silk and wool a beautiful ponceau colour. It is a position isomeride of orange No. I. In general the orthohydroxyazo-dyes of α-naphthol are red; the parazo-dyes are yellowish-brown.

$OH{\cdot}C_{10}H_5(SO_3H){\cdot}N_2{\cdot}Ph$ [1 : 4 : 2] is a ponceau colour,

$$OH{\cdot}C_{10}H_5(SO_3H){\cdot}\overset{\alpha}{N}_2{\cdot}C_{10}H_7{}^{\alpha}\ [1 : 4 : 2]$$

is an orseille red, $O\overset{\alpha}{H}{\cdot}C_{10}H_5(SO_3H){\cdot}N_2{\cdot}C_{10}H_7{}^{\beta}$ is a ponceau. $OH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_6{\cdot}SO_3H$ [1 : 2] (from β-naphthaquinone and the hydrazine of naphthionic acid) is a bluish orseille red, whilst the [1 : 4] compound (from diazonaphthionic acid and α-naphthol) is brown.

Orthophenylazo-α-naphtholmetacarboxylic acid,

$$OH{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4{\cdot}COOH\ [N_2 : COOH = 1 : 3],$$

is obtained by shaking β-naphthaquinone suspended in 10—15 times its weight of acetic acid with metahydrazinebenzoic acid suspended in water. It is necessary to use the pure hydrazinebenzoic acid. It is insoluble in water, but soluble in alkaline hydroxides and barium hydroxide, and dissolves in concentrated sulphuric acid to a reddish-brown liquid, which turns red on addition of a little water, and then precipitates the compound unchanged. It is insoluble in most solvents in the cold, and is purified by crystallisation from aniline;

from alcohol, it crystallises in prisms, coagulates at 200°, and melts at 260° with evolution of gas. It dyes silk and wool a bluish-red, and fibre mordanted with chromic oxide can be dyed with it. The *acetate*, $OAc\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot COOH$, is obtained by boiling the above compound with acetic anhydride and sodium acetate in a reflux apparatus. It is easily soluble in alcohol, sparingly in benzene and acetic acid, crystallises from benzene in yellowish-orange crystalline masses, melts at 210°, and gives a red solution with concentrated sulphuric acid.

The *isomeric para-compound* $[OH : N_2 = 1 : 4]$ is obtained by the action of diazotised amidobenzoic acid on α-naphthol. It is a black powder with a green, metallic lustre, dissolves easily with a brown colour in alcohol and aniline, and is insoluble in benzene. With concentrated sulphuric acid, it gives a bluish-violet coloration, which, on addition of water, changes to red. It imparts a brown colour to silk and wool in an acid bath and to cotton mordanted with chromic oxide in a neutral bath. E. C. R.

Molecular Change in the Formation of Disazo-compounds of α-Naphthol. By E. Noelting and E. Grandmougin (*Ber.*, **24**, 1601—1605).—In attempting to compare the disazo-compounds formed from the naphthaquinone hydrazone of metamidobenzoic acid and paramidobenzenesulphonic acid with diazobenzene with those from phenylazo-α-naphthol and the diazo-compound of amidobenzoic acid and sulphanilic acid respectively, a curious intramolecular change was observed to take place in the case of the latter reaction, and instead of the normal products, there were obtained phenyldisazo-α-naphthol, $OH\cdot C_{10}H_5(N_2Ph)_2$ [1 : 2 : 4], together with disazo-α-naphthol-metamidobenzoic acid, $OH\cdot C_{10}H_5(N_2\cdot C_6H_4\cdot COOH)_2$ [1 : 2 : 4], and disazo-α-naphthol-sulphanilic acid, $OH\cdot C_{10}H_5(N_2\cdot C_6H_4\cdot SO_3H)_2$ [1 : 2 : 4], respectively.

Diazobenzene Chloride and β-Naphthaquinonehydrazonebenzoic Acid.—Diazobenzene chloride (1 mol.) is added to an alkaline solution of β-naphthaquinonehydrazonebenzoic acid (1 mol.), and the combination completed by heating on the water-bath. The product is precipitated with acid and crystallised from aniline and then from alcohol. It is sparingly soluble in the ordinary solvents, crystallises in very minute needles, blackens at 200°, and decomposes at 245—246°. Analysis gave results corresponding with the formula

$$N_2Ph\cdot C_{10}H_5(OH)\cdot N_2\cdot C_6H_4\cdot COOH\ [= 4 : 1 : 2].$$

It is only a feeble acid, dissolves in warm alkalis and baryta-water, but precipitates on cooling, has only faint tinctorial powers, and yields a green solution with concentrated sulphuric acid. The *acetate* crystallises from benzene in slender, yellow needles, darkens at 200°, and decomposes at 229—230°.

Diazobenzene Chloride and β-Naphthaquinonehydrazonesulphanilic Acid.—The reaction takes place in the same way as the above. The sodium salt of the disazo-compound is obtained as a gelatinous precipitate. The free acid, $N_2Ph\cdot C_{10}H_5(OH)\cdot N_2\cdot C_6H_4\cdot SO_3H$ [= 4 : 1 : 2], is a brownish-red powder, sparingly soluble in cold water, easily in hot water. It dyes silk and wool in acid bath a garnet-brown shade.

Diazosulphanilic Acid and Phenylazo-α-naphthol.—Phenylazo-α-naphthol is obtained by the action of diazobenzene chloride (1 mol.) on a solution of α-naphthol (1 mol.) in sodium hydroxide (2 mols.). At the same time, an appreciable quantity of the disazo-compound is formed. The phenylazo-α-naphthol is precipitated from the alkaline solution, dissolved in barium hydroxide, again precipitated, and crystallised from alcohol or acetic acid. It melts at 206°. When diazosulphanilic acid (1 mol.) is mixed with benzeneazo-α-naphthol (1 mol.) and sodium hydroxide (2 mols.) and the combination completed on the water-bath, a large quantity of the substance remains undissolved, and the alkaline solution becomes dark reddish-brown. The undissolved compound was identified as benzenedisazo-α-naphthol. The alkaline liquid contained the disulphonic acid of benzenedisazo-α-naphthol. This latter is not precipitated by acids, so that it was not obtained in the pure state; but a preparation obtained by the action of 2 mols. of diazobenzenesulphonic acid on α-naphthol seemed to be identical with it.

Metadiazobenzoic Acid and Phenylazo-α-Naphthol.—The combination of the two compounds takes place easily; the product of the reaction is a mixture of phenyldisazonaphthol and disazonaphtholphenylcarboxylic acid. To separate these compounds, the mixture is acidified and the dry precipitate extracted with chloroform. Benzenedisazo-α-naphthol is dissolved. The undissolved residue dissolves easily in alcohol, but could not be obtained crystalline. It is purified by solution in soda and reprecipitation with acid, and is so obtained as a reddish-black powder which blackens at 250° and decomposes at 264°. It was similar in all respects to the compound obtained by the action of diazobenzoic acid (2 mols.) on α-naphthol.

E. C. R.

Constitution of the Hydrazone of β-Naphthaquinone. By E. Noelting and E. Grandmougin (*Ber.*, **24**, 1592—1597).—The authors have obtained results which tend to show that phenylazo-β-naphthol and the isomeric hydrazone of β-naphthaquinone are azo-compounds and not hydrazones.

β-Naphthaquinone phenylhydrazone is obtained as described by Zincke and Bindewald (*Ber.*, **17**, 3026). The yield is small, owing to the oxidising action of the β-naphthaquinone on the hydrazine; which latter is converted into benzene, whilst the quinone is converted into dinaphthyldiquinol. The phenylhydrazone melts at 138°, sublimes, like phenylazo-β-naphthol, in beautiful, orange-red needles with a green, metallic lustre, and is insoluble in cold alkali, but dissolves in the hot solvent and separates out unchanged on cooling. The sodium salt is obtained by dissolving the hydrazone in a methyl or ethyl alcoholic solution containing the theoretical quantity of sodium. The formula of the sodium salt is $ONa{\cdot}C_{10}H_6{\cdot}N_2{\cdot}Ph$, since, on reduction of the ethyl salt obtained from it, aniline is formed and not ethylaniline.

Phenyldisazo-α-naphthol is obtained by adding a solution of diazobenzene chloride to an ice-cold solution prepared by dissolving twice the theoretical quantity of sodium in alcohol and adding the hydrazone. The mixture is allowed to remain over night and the product filtered, dissolved in hot chloroform, and the solution mixed with absolute alcohol. It crystallises on cooling in slender, brown needles with a green lustre, melts at 193°, dissolves very sparingly in hot alkalis, easily in alcoholic sodium ethoxide, but is precipitated on addition of water. It is identical with the product obtained by Krohn by the action of diazobenzene chloride (2 mols.) on α-naphthol (*Ber.*, **21**, 3240). The *acetate*, $OAc{\cdot}C_{10}H_5(N_2Ph)_2$, is obtained by heating the disazo-compound with acetic anhydride and sodium acetate in a reflux apparatus until the colour changes from red to yellow. It crystallises from alcohol in beautiful, brown, prismatic needles, melts at 159—160°, decomposes at 200°, and dissolves in concentrated sulphuric acid with a green coloration. The *ethyl* salt, $OEt{\cdot}C_{10}H_5(N_2Ph)_2$, is obtained by adding an excess of ethyl iodide to a solution of the diazo-compound in the theoretical quantity of sodium ethoxide, and allowing the mixture to remain three weeks in the cold. It crystallises from alcohol in tufts of reddish-brown needles, and melts at 121°. The *methyl* salt crystallises in blue-black needles with a metallic lustre, and melts at 123°.

It was not possible to obtain a hydrazoneoxime by the action of hydroxylamine or its salts on the β-naphthaquinone hydrazone.

E. C. R.

Nitro-derivatives of Alizarin and Purpurin. By R. BRASCH (*Ber.*, **24**, 1610—1619).—*Diacetyl-α-nitroalizarin* is obtained by cautiously adding diacetylalizarin (1 part) to colourless nitric acid (2 parts; sp. gr. = 1·5) cooled with ice and salt, so that the temperature does not rise above zero; 1 part more of nitric acid is then added, and as soon as the product no longer gives the alizarin spectrum, the mixture is poured into iced water. It crystallises from acetic acid in beautiful, bright-yellow needles, melts at 194—195·5° (uncorr.), and is easily hydrolysed by cold soda solution.

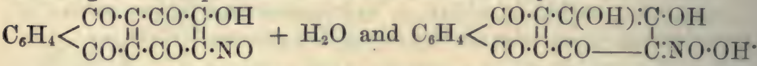
α-Nitroalizarin obtained by hydrolysis of the acetyl compound, crystallises from acetic acid in brownish-yellow, prismatic needles, and melts at 289° (uncorr.). The absorption spectra of α-nitroalizarin is very like that of alizarin.

α-Amidoalizarin is obtained by reducing the nitro-compound suspended in dilute ammonia with hydrogen sulphide. The amido-compound is precipitated with hydrochloric acid, dried, and freed from sulphur by extraction with carbon bisulphide. It is sparingly soluble in most solvents, and crystallises from acetic acid in dark-brown scales with a yellowish-green, metallic lustre. When treated with excess of nitrous acid, it is not completely converted into a diazo-compound, and on warming the diazotised mixture, purpurin is formed. If, however, the diazotised mixture be saturated with alkali and then warmed and extracted with ether, alizarin is obtained. β-Amidoalizarin on diazotisation did not yield a trace of purpurin, but only alizarin, which is contrary to the statement of Auerbach (*Das Anthracene*, 1880, p. 152).

Strecker (*Zeit. Chem.*, **4**, 264) has shown that when alizarin is treated with fuming nitric acid, at first an unstable compound is formed, which, in the presence of water, is easily converted into nitroalizarin. This unstable compound is also obtained from purpurin by the action of fuming nitric acid, and has the same percentage composition as nitrohydroxyalizarin. The author names this unstable compound pseudonitropurpurin and the nitrohydroxyalizarin nitropurpurin.

Pseudonitropurpurin is obtained by mixing alizarin with fuming nitric acid so as to form a thin paste, and allowing the mixture to remain until no alizarin can be detected with the spectroscope. The mixture is poured on to ice, diluted with water, filtered, and washed with iced water. The yellow compound begins to dissolve as soon as all the acid is washed out, and decomposes into nitropurpurin.

It is purified by drying in thin layers in a vacuum and extracting the nitropurpurin with absolute ether. It is a bright-yellow mass, which is stable when pure and dry, is converted into nitropurpurin when heated with water, and dissolves in cold soda solution to a brownish-yellow solution, which goes red on warming, owing to the formation of nitropurpurin. In concentrated sodium hydroxide it is fairly stable, but turns red at once on the addition of water. The author gives two probable formulæ for this compound,



$$C_6H_4<\begin{matrix}CO\cdot C\cdot CO\cdot C\cdot OH\\ \quad\; \| \qquad\;\; \| \\ CO\cdot C\cdot CO\cdot C\cdot NO\end{matrix} + H_2O \text{ and } C_6H_4<\begin{matrix}CO\cdot C\cdot C(OH):C\cdot OH\\ \quad\; \| \qquad\qquad\quad | \\ CO\cdot C\cdot CO\text{——}C:NO\cdot OH\end{matrix}\cdot$$

Nitropurpurin $[(OH)_2 : NO_2 : OH = 1 : 2 : 3 : 4]$ is obtained from pseudonitropurpurin by boiling with water or alkali. It is very like purpurin, gives the same colours with chromium, iron, and alumina mordants, and dissolves in sulphuric acid with a yellowish-red; purpurin gives a carmine-red. If purpurin is cautiously added to a large quantity of well-cooled fuming nitric acid, a yellowish-brown compound is deposited which is identical with pseudonitropurpurin and is easily converted into nitropurpurin. β-Nitroalizarin $[(OH)_2NO_2 = 1 : 2 : 3]$, when treated with 7 parts of nitric acid (1·5) at the ordinary temperature, yields the same intermediate compound and then nitropurpurin. The same nitropurpurin is also obtained by the action of nitric acid on α-nitropurpurin $[(OH)_2NO_2 = 1 : 2 : 4]$.

Amidopurpurin is obtained by reduction of the nitro-compound with ammonium sulphide. It is very sparingly soluble in most solvents, dissolves in concentrated sulphuric acid with a reddish-yellow, and gives blackish colours with iron and chromium mordants, red with alumina mordants. E. C. R.

Terpenes and Camphors. By O. WALLACH (*Ber.*, **24**, 1525—1579).—The paper contains an account of the most important results obtained up to the present time.

The terpene-like hydrocarbons can be divided according to their empirical formulæ into three classes:—(1) Hemiterpenes or pentenes, C_5H_8. (2) Terpenes, $C_{10}H_{16}$. (3) Polyterpenes, $(C_5H_8)_n$. The terpenes at higher temperatures split up into unsaturated hydrocarbons of the series C_5H_8, whose best known representative is isoprene. Isoprene can undergo polymerisation into $C_{10}H_{16}$, and a further polymerisation into $C_{15}H_{24}, C_{20}H_{32}$, &c. Ordinary terpene is also polymerisable into such polyterpenes.

The present paper deals with the terpenes $C_{10}H_{16}$. At present the following terpenes are known:—(1) Pinene, (2) camphene, (3) fenchene, (4) limonene, (5) dipentene, (6) sylvestrene, (7) phellandrene, (8) terpinene, (9) terpinolene. *Pinene* forms the main constituent of ordinary turpentine oil, occurs as an essential ingredient of the ethereal oils of most pines, and in greater or smaller quantity in many other ethereal oils. *Camphene* is important on account of its near relation to camphor. It is obtained from camphor through borneol or from pinene. It does not appear to occur in nature. *Fenchene* is closely related to camphene, and is obtained in a similar way from fenchone, a compound isomeric with camphor. *Limonene*, one of the most widely diffused terpenes, occurs in the ethereal oils of the *Aurantiaceæ*, in orange-peel oil, in oil of lemons, bergamot, cummin, dill, oil of *Erigeron canadense*, and in the oil of fir needles. *Dipentene* is closely related to limonene. It is formed from limonene and pinene by the action of heat or of acids, and occurs in oil of camphor and elemi, in Russian and Swedish turpentine, and is formed together with isoprene by the dry distillation of caoutchouc, and as a bye-product in the formation of cineole, terpene hydrate, and terpineole. *Sylvestrene* occurs in Russian and Swedish turpentine. *Phellandrene* occurs in the oils of bitter fennel and water fennel, elemi, and eucalyptus. *Terpinene* is a product of the molecular change of other terpenes. It occurs naturally in oil of cardamom. *Terpinolene* is only slightly known.

The terpenes exist in physically different modifications. Thus the pinene from American turpentine is dextro-rotatory, that from French turpentine lævo-rotatory. By the action of mineral acids or by heat, the optically-active terpenes are rendered optically inactive. The inactive modifications are obtained by mixing equal proportions of the optical antipodes. Active terpenes as a rule give active derivatives. The inactive pinene, camphene, and phellandrene compounds are indistinguishable, except as regards optical properties, from the corresponding active compounds. The inactive modification of limonene is quite different from the active modification, and was taken for a distinct compound and called dipentene. Dipentene, however, stands in the same relation to dextro- and lævo-limonene as racemic acid does to dextro- and lævo-tartaric acids. Sylvestrene is only known in the dextro-modification; and fenchene, terpinene, and terpinolene in the inactive modifications. Camphene is the only terpene which is solid; it melts at 50°. Pinene, camphene, and fenchene boil at 160°, and have a high specific gravity (about 0·86). Limonene, dipentene, and sylvestrene boil at 175°, and have a low specific gravity (about 0·846 at 20°). Those terpenes which from chemical considerations are held to contain one ethylene bond, and those containing two ethylene bonds, show amongst one another a concordant molecular refraction.

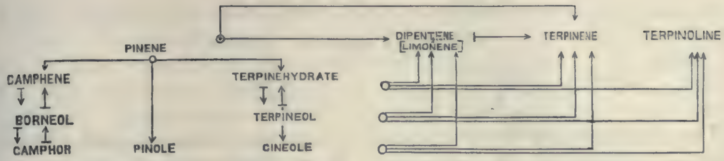
The terpenes are unsaturated compounds, and differ in their capacity for combining with halogen hydrides. If dry hydrogen chloride be led into dry pinene, a molecule of the gas is added, and a saturated compound, pinene hydrochloride, is obtained, which melts at 125° and boils at 207—208°. Camphene in like manner unites with 1 mol. of hydrogen chloride to form camphene hydrochloride, which resembles pinene hydrochloride. It, however, easily loses hydrogen chloride with formation of camphene, whereas pinene hydrochloride loses hydrogen chloride with difficulty, and then yields camphene and not pinene. Dry limonene, when treated with dry hydrogen chloride, yields a liquid hydrochloride, $C_{10}H_{16},HCl$, which is not, however, saturated, and takes up moist hydrogen chloride to form the dihydrochloride $C_{10}H_{16},2HCl$. Dipentene and sylvestrene behave like limonene towards hydrogen chloride.

The bromo-additive compounds are also important as a means of characterising the terpenes. Pinene unites with 1 mol. of bromine, and yields a saturated dibromide, $C_{10}H_{16}Br_2$ (m. p. 169—170°). A bromine additive compound of camphene is not known. The compound $C_{10}H_{16}Br_2$, from fenchene, is liquid. Limonene, dipentene, sylvestrene, terpinolene unite with 4 atoms of bromine to form compounds of the formula $C_{10}H_{16}Br_4$. These bromides melt at 104—105°, 124—125°, 135°, and 116° respectively. From the above results, it is seen that two terpene groups exist. The members of one contain one ethylene bond, and give saturated compounds with 1 mol. of halogen and halogen hydride; the members of the second contain two ethylene bonds, and combine with 1 mol. of halogen hydride to form unsaturated compounds, and with 2 mols. of halogen or halogen hydride to form saturated compounds.

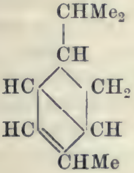
Well characterised compounds are obtained by the action of the oxides of nitrogen and their derivatives on the terpenes. Phellandrene combines with nitrogen trioxide, N_2O_3, to yield phellandrene nitrite, $C_{10}H_{16}N_2O_3$ (m. p. 102°). Terpinene combines in a similar way with nitrous acid, and yields terpinene nitrosite, $C_{10}H_{16}N_2O_3$, which crystallises in transparent, monosymmetric prisms and melts at 155°. The other terpenes do not give crystalline compounds with N_2O_3, but they yield important compounds with nitrosyl chloride, NOCl. These compounds are best prepared by adding ethyl nitrite or amyl nitrite to an acetic or alcoholic solution of the terpene, and passing hydrogen chloride into the well-cooled mixture. The compounds have the formula $C_{10}H_{16}Cl{\cdot}NO$, and correspond with terpinene nitrosite,

$$NO{\cdot}C_{10}H_{16}{\cdot}ONO.$$

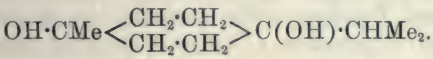
If the terpene be mixed with alkyl nitrite and nitric acid, instead of alkyl nitrite and hydrogen chloride, then an analogous nitrosate, $NO{\cdot}C_{10}H_{16}{\cdot}ONO_2$, is formed. The unsaturated hydrochlorides of the terpenes with two ethylene bonds easily form nitrochlorides and nitrosates of the composition $C_{10}H_{16}{\cdot}ClNO,HCl$ and $C_{10}H_{16}{\cdot}ClNO,HONO_2$. These compounds are not all very stable, and are decomposed when warmed. When treated with organic bases they are easily converted into nitrolamines, $NO{\cdot}C_{10}H_{16}{\cdot}NHR$. Such bases have been obtained from pinene, limonene, dipentene, sylvestrene, and terpinene; they are well crystallised and stable compounds, and give sharp melting points. When hydrochloric acid is withdrawn from the nitrosochlorides, nitroso-compounds of the formula $C_{10}H_{15}NO$ are obtained which crystallise well. A table is given summarising the properties of the terpenes and their derivatives. The remainder of the paper deals with the constitution of the terpenes. The terpenes are convertible into one another, as is shown by the following table.



Pinene is distinguished by the readiness with which it is converted into other terpenes. The author puts forward the formula

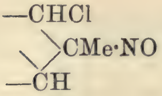


for pinene, and maintains that it explains most of its reactions. The assumption of the existence of a diagonal bond is necessary, and obtains support from the fact that pinene hydrochloride by loss of hydrochloric acid yields a hydrocarbon, which by addition of hydrogen chloride is not again converted into pinene hydrochloride, and that pinene hydrochloride loses HCl with greater difficulty than its isomerides camphene, limonene, and dipentene hydrochlorides. When heated to a high temperature, pinene, which contains only one ethylene bond, is converted into dipentene, which contains two ethylene bonds. In the presence of dilute acids, it is converted into compounds which must be considered as derivatives of dipentene, and are obtainable from dipentene directly. Pinene, when treated with moist hydrogen chloride, does not yield pinene hydrochloride, but dipentene hydrochloride; with dilute nitric acid, it yields terpine. Dry reagents first break the ethylene bond in pinene, as is seen in the formation of pinene hydrochloride by the action of dry hydrogen chloride. When treated with moist acids, it not only yields dipentene derivatives but also terpinene, terpinolene, terpineole, and cineole. These compounds are, however, formed by a secondary reaction from terpine, $C_{10}H_{20}O_2$, or terpine hydrate, $C_{10}H_{20}O_2 + H_2O$. The formation of these compounds is then explained by giving to terpine the formula

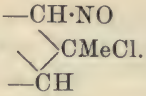


$$OH{\cdot}CMe<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>C(OH){\cdot}CHMe_2.$$

Pinene.—The formula of pinene given above explains its most important reactions, its conversion into dipentene, terpineole, terpine hydrate, and cineole, and the splitting of the molecule to give isopsene. That pinene contains only one ethylene bond follows from the saturated nature of the hydrochloride, hydrobromide, and the dibromide. The molecular refraction also agrees with this supposition. Pinene nitrosochloride is also a saturated compound. Two formulæ are possible, containing the groupings—


I.

and


II.

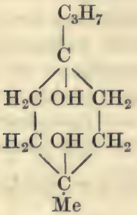
The author is inclined to consider formula I as most probable, from a consideration of its reactions. It is distinguished by its great stability, relatively to the other terpene nitrosochlorides. With fatty bases, it yields a nitrolamine; with aromatic bases, no such reaction takes place, but inactive pinene is produced with the formation of amidoazo-compounds. By this reaction it is possible to prepare chemically pure pinene. With inorganic bases, a different reaction takes place; thus alcoholic potash eliminates hydrogen chloride and nitrosopinene, $C_{10}H_{15}NO$, is formed. The latter differs from the analogous isomeric nitroso-compounds of other terpenes. Thus nitrosolimonene when warmed with dilute acid yields hydroxylamine and carvole, $C_{10}H_{14}O$, whilst nitrosopinene is not attacked by acids; it can even be warmed with concentrated sulphuric acid, and on addition of water is precipitated unchanged. This difference is explained if the isomeric compounds contain the group $=$NOH combined directly with a carbon atom, whilst nitrosopinene contains the group —N:O. If the above formula be accepted for pinene nitrosochloride, one must assume that in the production of nitrosopinene the chlorine atom goes out with the para-hydrogen atom. Two formulæ are then possible for nitrosopinene, of which the author favours one with two diagonal bonds. When nitrosopinene is reduced with zinc and acetic acid, it yields pinylamine, $C_{10}H_{15}\cdot NH_2$. If pinylamine hydrochloride is heated above its melting point, it decomposes into ammonium chloride and cymene. A similar decomposition takes place in the case of pinene dibromide, which, on heating, also yields paraisopropylmethylbenzene. In the bye-products obtained in the formation of pinene nitrosochloride, pinole, $C_{10}H_{16}O$, is found. The latter yields a series of well-characterised derivatives of which the most important is pinole hydrate, $C_{10}H_{16}O,HOH$ (m. p. 131°). Pinole hydrate is converted by dilute acids into pinole, and is identical with the compound obtained by the oxidation of moist turpentine under the influence of sunlight. Pinole, when oxidised with potassium permanganate, yields terebic acid, $C_7H_{10}O_4$; pinole hydrate and pinole glycol, however, yield terpenylic acid, $C_8H_{12}O_4$, that is, those two acids are obtained which are formed by the direct oxidation of pinene.

Camphene and Fenchene.—The constitution of camphene depends closely on that of camphor. Camphor is easily converted into camphene, either by reduction to borneol and elimination of the elements of water, or by converting the borneol into bornyl chloride and eliminating hydrogen chloride. The behaviour of camphor is best explained by the formula proposed by Bredt, and camphene would then have an analogous formula. This formula, although it explains the behaviour of camphene, does not so easily explain its formation from pinene hydrochloride.

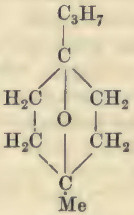
In many fennel oils a liquid, camphor-like substance occurs. This compound is called fenchone, and is isomeric with camphor, and, moreover, undergoes the same characteristic reactions (compare p. 1086). It yields a well-crystallised oxime, $C_{10}H_{16}\colon NOH$, which behaves like camphoroxime towards dilute acids. It gives a nitrile-like compound, $C_9H_{15}\cdot CN$, an isoamide, $C_9H_{15}\cdot CONH_2$, a base, $C_9H_{15}\cdot CH_2\cdot NH_2$, and an acid, $C_9H_{15}\cdot COOH$, which are like the corresponding compounds from camphoroxime, and are isomeric with them. Fenchone, on reduction, yields fenchyl alcohol, and from this one obtains fenchyl chloride and fenchene, $C_{10}H_{16}$. These compounds are isomeric with borneol, bornyl chloride, and camphene. A table is given containing all the known compounds of camphene and fenchene. In general properties fenchene also resembles camphene, namely, in smell, high specific gravity, molecular refraction, and boiling point; it is, however, a liquid, whilst camphene is a solid. Fenchone, on oxidation with potassium permanganate, yields dimethylmalonic acid, $CMe_2(COOH)_2$, and acetic acid, but not camphoric acid. The formation of dimethylmalonic acid points to the presence in fenchene of the grouping $CMe_2{<}\begin{smallmatrix}C\cdot\\ C\cdot\end{smallmatrix}$, whilst camphor contains the isopropyl group and the grouping $CHMe_2\cdot C{<}\begin{smallmatrix}C\cdot\\ C\cdot\end{smallmatrix}$.

Limonene and Dipentene.—These two hydrocarbons probably have the same chemical structure, dipentene being the racemic modification of lævo- and dextro-limonene. Limonene combines easily with nitrosyl chloride; two compounds, α- and β-nitrosochlorides, are formed from both lævo- and dextro-limonene, so that four isomeric limonene nitrosochlorides exist. The β-compounds have a somewhat smaller rotatory power than the α-compounds. The author thinks these two modifications are identical as regards structure, and that the difference is due to polymerisation. Dextro- and lævo-limonene α-nitrosochlorides each yield two isomeric nitrolamines, of which two have the same melting point but are of opposite rotatory power. If two of these optical antipodes be recrystallised together in equal proportions, an inactive dipentene derivative is obtained. Limonene, from its behaviour towards halogens and halogen hydrides, has certainly two ethylene bonds. Goldschmidt has shown that carvoxime is identical with nitrosolimonene, and hence limonene may be considered to be hydrocymene. However, dipentene dihydrobromide (m. p. 64°) can be converted into a tribromide, $C_{10}H_{17}Br_3$ (m. p. 110°). The latter, when boiled with alcoholic potash, is converted into an unsaturated compound, $C_{10}H_{14}$, isomeric with cymene, which unites with bromine to form a well-characterised tetrabromide melting at 154°. Formulæ are given as far as possible in accordance with the above results. The three compounds terpineole, terpine, and cineole show the relation between pinene and limonene and dipentene. Terpine, $C_{10}H_{20}O_2$, which crystallises with 1 mol. of water to form terpine hydrate, has already had a formula assigned to it which explains its reactions. Terpineole and terpine hydrate are closely related to limonene and dipentene hydrochloride and to dipentene dihydrochloride, since when dipentene dihydrochloride is allowed to remain in contact with water, terpine hydrate is formed.

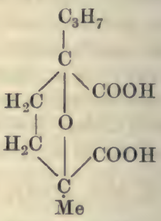
Cineole, $C_{10}H_{18}O$, occurs in many ethereal oils. It gives characteristic additive compounds with bromine, iodine, hydrogen chloride, and hydrogen bromide. By the action of dehydrating agents, it is converted into dipentene. On oxidation with potassium permanganate, it is converted into cineolic acid, which easily passes into its anhydride. When the latter is distilled, it loses CO_2 and CO, and yields a compound $C_8H_{14}O$, which is easily converted into dihydrometaxylene. Cineole can be obtained from terpine hydrate and terpineole. The following formulæ are given showing the relation of the above compounds:—



Terpine.



Cineole.



Cineolic Acid.

Nothing is known about the constitution of *sylvestrene*. In its physical and chemical properties it most closely resembles dextrolimonene. It contains two ethylene bonds. *Terpinolene* also contains two ethylene bonds, and probably only differs from dipentene in the relative position of these bonds.

Terpinene and *phellandrene* both combine with nitrogen trioxide to form compounds of the formula $C_{10}H_{16}N_2O_3$. The two compounds so obtained are, however, quite different. Terpinene nitrosite, when treated with fatty bases or ammonia, yields well-characterised nitrolamines. Both terpinene nitrosite and the nitrolamines behave in some cases as if they contained the group —NO; in other reactions they behave as if they contained the group $\equiv$NOH. Phellandrene nitrite is a somewhat unstable compound, and is not capable of yielding nitrolamines. On reduction, it yields a diamine which points to the constitution $C_{10}H_{16}<\begin{matrix}NO\\NO_2\end{matrix}$. The isomeric relation of terpinene and phellandrene to one another and to other terpenes has not been determined. Terpinene has probably an ethylene bond in the side chain. Phellandrene, which is easily convertible into cymene, is possibly a fatty compound.

The author draws attention to the similarity of some indene compounds to the terpenes.

E. C. R.

Presence of Ethylene Linkages in Terpenes. By G. WAGNER (*Ber.*, **24**, 1682—1684).—The paper is a reply to Markovnikoff's criticism (*Ber.*, **24**, 67) of a previous paper by the author.

Terebenthene. By R. VARET (*Compt. rend.*, **112**, 732—734).—When anhydrous aluminium chloride is added to terebenthene, there is a slight development of heat, but no further change, even after several hours. If, however, the mixture is heated, or a few drops of benzene is added, there is a very violent reaction, with formation of tarry products containing cymene and toluene. If the terebenthene is dissolved in 3 vols. of carbon bisulphide, and aluminium chloride is added gradually to the cooled liquid, the reaction is still energetic, and a blood-red solid is obtained, consisting chiefly of metaterebenthene and tetraterebenthene, with smaller quantities of cymene, colophene, and other hydrocarbons. It follows that the action of aluminium chloride on terebenthene is similar to that of antimony chloride.

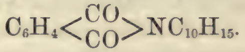
When terebenthene is added gradually to a solution of bromine in 3 vols. of carbon bisulphide holding aluminium chloride in suspension and cooled below 0°, there is an energetic reaction with evolution of hydrogen bromide. After 136 parts of terebenthene have been added for every 800 parts of bromine, the liquid is allowed to remain until evolution of hydrogen bromide ceases, and is then treated with water and sodium hydroxide solution, and distilled. A small quantity of isopropyl bromide is obtained, but the product consists of heavy, tarry compounds, formed by the action of the bromine on the products of the polymerisation of the terebenthene. Terebenthene, when treated with bromine and aluminium chloride, does not, like cymene, split up into isopropyl bromide and a bromine derivative of toluene. The small quantity of isopropyl bromide obtained results from the action of the bromine on the cymene formed during the polymerisation of the terebenthene. C. H. B.

Terpene in the Oil from Compressed Gas. By A. ETARD and P. LAMBERT (*Compt. rend.*, **112**, 945—947).—In the compression of the gas obtained by the pyrogenic decomposition of heavy paraffin oils, a quantity of volatile liquid condenses. If this liquid is fractionated, the fraction 140—190° shows no constant boiling point. By rapid fractionation, however, a hydrocarbon, C_5H_6, is obtained, which boils at 42·5°; sp. gr. = 0·803; vapour density 2·45. This hydrocarbon, *pyropentylene*, polymerises at the ordinary temperature, and forms a solid compound, *dipyropentylene*, $C_{10}H_{12}$, which has all the principal properties of the terpenes. Polymerisation proceeds regularly, and can be followed by determining the sp. gr. When the dipyropentylene is heated, pyropentylene is again formed.

Pyropentylene has a very pungent taste and a peculiar odour. It is not affected by ammoniacal silver or cuprous solutions, but with a concentrated aqueous solution of silver nitrate, it yields a white, acicular precipitate, and it reduces an ammoniacal silver solution containing potash. With aqueous sulphurous acid, it yields a white, crystalline compound, $C_{10}H_{12},2H_2SO_3$, almost insoluble in all reagents except alkalis, and with a remarkable tendency to retain any iron that was present in the reagents. With haloïd acids, pyropentylene resinifies rapidly or explodes; oxidising agents destroy it completely; bromine alone yields liquid products.

Pyropentylene is not identical with valylene or pirylene; it is isomeric with these hydrocarbons, and is more closely related to the terpenes. C. H. B.

Action of Phthalic Anhydride on Amidoterebenthene. By L. Pesci (*Gazzetta*, **21**, 1—4).—*Pinenephthalimide*,



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NC_{10}H_{15}.$$

—When amidoterebenthene (10 grams) is poured on to powdered phthalic anhydride (12 grams), a very energetic reaction ensues; the mass is then allowed to cool, and subsequently reheated at 170°, until the reaction is completed; the portion of the product insoluble in water consists of pinenephthalimide, which, after purification, crystallises from light petroleum in colourless nodules, composed of rectangular tables. It melts at 99—100°, and dissolves readily in alcohol, chloroform, and ether. It is lævorotatory, $[\alpha]_D = -35\cdot38$.

Pinenephthalamic Acid, $COOH\cdot C_6H_4\cdot CO\cdot NH\cdot C_{10}H_{15}$.—The potassium salt of this acid is formed on dissolving pinenephthalimide in a hot solution of potash. It crystallises in thin, colourless needles, readily soluble in hot water. The acid obtained by decomposing this salt with hydrochloric acid, when pure, crystallises from chloroform on the addition of light petroleum in nodules composed of thin, colourless needles. It melts at first at 109—111°, but if kept for a few days the melting point falls to 101°. The *silver salt*,

$$COOAg\cdot C_6H_4\cdot CO\cdot NH\cdot C_{10}H_{15},$$

is a white, amorphous compound. S. B. A. A.

New Compounds of the Camphor Series and a New Terpene. By O. Wallach (*Annalen*, **263**, 129—156).—A further investigation of the compound previously described as fenchole (this vol., p. 218), but which is, perhaps, better termed *fenchone*, has brought to light numerous additional points of resemblance between this substance and its isomeride, camphor; but what the relationship between the two compounds really is, remains at present unsolved.

Fenchone can be easily obtained in a state of purity by converting it into the crystalline alcohol described below, then warming the latter with nitric acid until oxidation is at an end, and distilling the regenerated fenchone with steam; an even simpler method is to warm the crude oil, obtained by fractional distillation, with concentrated nitric acid (3 parts), until all the impurities are destroyed. The pure compound boils at 192—193°, and gradually solidifies, when kept at a low temperature, to a mass of very hard crystals, which melt at 5—6° to a liquid of sp. gr. 0·9465 at 19°; its refraction is $[n]_D = 1\cdot46306$ at 19°, from which the molecular refractive energy is found to be 44·23, the calculated value for a compound of the composition $C_{10}H_{16}O$, containing no double linking, being 44·11. The specific rotatory power of fenchone, purified by the methods given above, is $[\alpha]_D = 71\cdot83°$. It combines with bromine, yielding a crystalline, unstable additive compound, which is decomposed by alkalis with liberation of fenchone; iodine, phosphorus pentachloride, phosphoric anhydride, and phosphorus sulphide, have an action on fenchone similar to that on camphor, but the products have not yet been thoroughly investigated. Fenchone dissolves moderately easily in cold concentrated hydrochloric acid, and with cold sulphuric acid it seems to give an unstable additive compound, which is decomposed by water; it is only very slowly destroyed by boiling fuming nitric acid, being thereby converted into organic acids and a heavy oil, which is insoluble in alkalis. It is slowly oxidised by a warm solution of potassium permanganate, yielding dimethylmalonic acid, acetic acid, and oxalic acid; its physiological action is very similar to that of camphor.

The melting point of fenchonoxime (*loc. cit.*) depends, to a very considerable extent, on the conditions of the experiment, and sometimes, when the oxime is heated quickly, the temperature rises to 164—165° before it is completely melted; fenchonoxime is volatile with steam, sublimes readily, and boils at about 240° with only slight decomposition when heated quickly; it is insoluble in soda, and its specific rotatory power in alcoholic solution is $[\alpha]_D = 65{\cdot}94°$.

The anhydride of the oxime (*loc. cit.*) has a sp. gr. of 0·898 at 20°; its specific rotatory power is $[\alpha]_D = 43{\cdot}31°$ and its refraction $n_D = 1{\cdot}46108$ at 20°; it forms a crystalline compound with hydriodic acid.

A *base* of the composition $C_{10}H_{17}{\cdot}NH_2$, isomeric with fenchylamine (see below), is formed when the anhydride of the oxime is reduced with sodium and alcohol; when the product is treated with hydrogen chloride in ethereal solution, it behaves like an unsaturated compound, and forms a salt of the composition $C_{10}H_{19}N,2HCl$; the *platinochloride* has the composition $(C_{10}H_{19}N)_2,H_2PtCl_6$.

Formylfenchylamine, $C_{10}H_{17}{\cdot}NH{\cdot}CHO$, is obtained when fenchone is heated with ammonium formate at 220—250° for three hours; it crystallises from water or dilute alcohol in lustrous plates, and seems to melt at 87°, but portions remain unliquefied until the temperature rises to 112°.

Fenchylamine, $C_{10}H_{17}{\cdot}NH_2$, prepared by boiling the formyl derivative with concentrated hydrochloric acid, and decomposing the salt thus produced with alkalis, is a colourless oil, of sp. gr. 0·9095 at 22°, and boiling at 195°; it has an odour recalling both that of piperidine and that of benzylamine, and it absorbs carbonic anhydride from the air, forming a solid carbonate; its specific rotatory power in alcoholic solution is $[\alpha]_D = -24{\cdot}63°$. The *hydrochloride*, $C_{10}H_{17}{\cdot}NH_2,HCl$, crystallises from water and alcohol in well-defined, transparent prisms. The *platinochloride*, $(C_{10}H_{17}{\cdot}NH_2)_2,H_2PtCl_6$, crystallises from water in long prisms, and effloresces when kept over sulphuric acid. The *sulphate* crystallises in needles or plates, and is not very readily soluble; the *nitrate*, the *benzoyl* derivative melting at 89·5°, and the *acetyl* derivative melting at 92° are easily obtained in crystals. When the hydrochloride of the base is treated with sodium nitrite, a neutral oil, which is neither fenchyl alcohol nor a diazo-compound, is obtained.

Benzylidenefenchylamine, $C_{10}H_{17}{\cdot}N{:}CHPh$, is formed with development of heat when the base is treated with benzaldehyde; it melts at 41·5°.

Fenchyl alcohol, $C_{10}H_{17}{\cdot}OH$, is obtained when fenchone is reduced with sodium and alcohol; the yield is quantitative. It is a colourless, crystalline compound, melts at 40—41°, boils at 201°, and has a sp. gr. of 0·933 at 50°; it is readily volatile with steam, and dissolves freely in alcohol, ether, light petroleum, and ethyl acetate, but is insoluble in water. Its specific rotatory power in alcoholic solution is $[\alpha]_D = -10·35°$; on oxidation with nitric acid, it is reconverted into fenchone.

Fenchyl chloride, $C_{10}H_{17}Cl$, prepared by treating the alcohol with phosphorus pentachloride in light petroleum solution, boils at 84—86° under a pressure of 14 mm., and is readily volatile with steam; its sp. gr. is about 0·9830 at 21°.

Fenchene, $C_{10}H_{16}$, is obtained, together with phenylfenchylamine (see below), when fenchyl chloride is heated with aniline; when the reaction is at an end, the solution is mixed with acetic acid, and the fenchene isolated by distillation with steam. The hydrocarbon boils at 158—160°, is optically inactive, and its sp. gr. is 0·864 at 20°; its refraction is $[n]_D = 1·4690$ at 20°, from which the molecular refractive energy is found to be 43·84, the calculated value for $C_{10}H_{16}$ $|^{=}$ being 43·54. It combines readily with bromine in glacial acid solution, yielding, apparently, an unstable dibromide of the composition $C_{10}H_{16}Br_2$; it is moderately easily oxidised by potassium permanganate, yielding an acid of the composition $C_{10}H_{16}O_3$, which melts at 137—138°, and forms a sparingly soluble silver salt, $C_{10}H_{15}O_3Ag$. It differs from other terpenes in being comparatively stable towards concentrated nitric acid, oxidation taking place only on warming.

Phenylfenchylamine, $C_{10}H_{17}·NHPh$, crystallises from alcohol in large, colourless needles, and melts at 93—94°. F. S. K.

Pyrogenic Conversion of Camphosulphophenols into Ordinary Phenols. By P. CAZENEUVE (*Compt. rend.*, **112**, 730—732).—A mixture of the barium salts of the five camphosulphophenols previously described, when subjected to dry distillation, yields water; sulphur; gaseous products, consisting of hydrogen sulphide, sulphurous anhydride, carbonic anhydride, methane, with a small quantity of propane or propylene; a small quantity of hydrocarbons, probably chiefly paracymene; and homologues of ordinary phenol in quantity amounting to 25 per cent. of the camphosulphophenols.

The phenols boiling below 210° consist of orthocresol (m. p. 31°, b. p. 186°) and metacresol, without any trace of ordinary phenol. The first fractions of the portion boiling at 210—235° have the composition of mixtures of cresols with propylphenols, whilst the later fractions have the composition of mixtures of propylphenols with cymophenols. The products seem to contain neither thymol, carvacrol, nor carvol. When heated with hydrochloric acid at 130° for four hours, neither methyl chloride nor any other alkyl chloride is obtained, and hence alkyl ethers are absent. The composition of the products and their stability when exposed to air and light point to the absence of polymerides. C. H. B.

Morrenole. By P. ARATA and C. GELZER (*Ber.*, **24**, 1851—1853).—The recently expressed juice of the fruit of *Morrenia brachystephana* is light yellow, and coagulates after remaining for 24 hours; the liquid portion is separated, boiled, filtered, and evaporated to dryness, and the residue extracted with alcohol; the solution thus obtained contains considerable quantities of morrenine (compare this vol., p. 1122).

The coagulated portion of the juice is digested with alcohol; a yellow resin remains, which smells of caoutchouc, and is soluble in carbon bisulphide. From the alcoholic solution, colourless crystals are deposited on cooling, which melt at 168°, are insoluble in water, but readily dissolve in ether, light petroleum, and mineral acids. The compound is termed *morrenole*, has the formula $C_{14}H_{22}O$ or $C_{15}H_{24}O$, and is analogous to cynanchole, from *Cynanchum acutum*, and to asclepion, from *Asclepia Syriaca*. J. B. T.

Aspergillin, a Vegetable Hæmatin. By G. LINOSSIER (*Compt. rend.*, **112**, 807—808).—Phipson's palmellin is rose-red, crystalline, and soluble in water, forming a dichroic solution which is rose-red by transmitted light, orange-yellow by reflected light. The solution is coagulated by heat, by ammonia, potash, or alcohol, but not by hydrochloric acid. When burnt, it leaves an ash containing calcium, chlorine, and iron.

The author's aspergillin is black, amorphous, and insoluble in water, but soluble in ammonia or potash, forming solutions which are not coagulated by heat or by alcohol. It is precipitated by hydrochloric acid. When burnt, it leaves a residue consisting of ferric oxide.

It is clear therefore that aspergillin is not identical with palmellin, and that the latter is not analogous to hæmatin (compare this vol., p. 845). C. H. B.

Humic Compounds. By BERTHELOT and G. ANDRÉ (*Compt. rend.*, **112**, 916—922).—The results described in this paper were obtained with artificial humic compounds. 1500 grams of sugar, boiled for a long time with concentrated hydrochloric acid, gave 236 grams of humic matter insoluble in water; when dried at 100°, it had the composition C, 66·41; H, 4·57; O, 29·02 = 100, which agrees with the formula $C_{18}H_{14}O_6$. Another preparation contained C, 63·91; H, 4·58; O, 31·51 = 100, which agrees with the formula $C_{18}H_{16}O_7$; the product obtained by the action of hydrochloric acid on the alkali salts has the same composition. The first compound is *humic anhydride;* the second is the true *humic acid.* Both compounds when left in contact with water swell up and acquire a gelatinous consistence, in this respect resembling colloïds. In presence of excess of potash, even in somewhat dilute solution, humic acid yields an insoluble colloïdal salt, $C_{18}H_{13}K_3O_7 + nH_2O$, which is decomposed by prolonged washing with water, two-thirds of the alkali being removed, whilst a salt, $C_{18}H_{15}KO_7$, is left. This last salt is formed when humic acid or the anhydride is left in contact with even a very dilute solution of potash; it is but slightly decomposed by water, even after prolonged boiling. Carbonic acid is practically without effect in the cold, but dilute hydrochloric acid removes the whole of the potassium. On the other hand, the anhydride, or acid, slightly decomposes a solution of potassium chloride with liberation of a small quantity of hydrochloric acid.

With sodium hydroxide, humic anhydride forms a compound,

$C_{18}H_{15}NaO_7$, which is insoluble, and in presence of excess of soda another salt is formed, containing not quite three times as much sodium. The latter compound loses alkali when washed with water, and is converted into the first salt. Barium hydroxide and calcium hydroxide behave similarly, forming two salts, one of which is decomposed by water.

In contact with excess of dilute ammonia, humic anhydride forms an insoluble, gelatinous compound containing 4 mols. NH_3. The product seems to be an acid amide; it does not lose ammonia at 40° in a current of hydrogen; at 100°, there is a distinct loss of nitrogen, and if the residue is boiled with magnesia and water, ammonia is evolved, but all the nitrogen is not expelled.

When heated with ammonia in sealed tubes at 100°, humic anhydride combines with about 9 per cent. of ammonia, and forms an insoluble product which can be dried at 100°, and does not lose all its nitrogen when boiled with magnesia. C. H. B.

Constitution of Rings containing Five Atoms. By E. BAMBERGER (*Ber.*, **24**, 1758—1764).—Stohmann and Kleber have shown (this vol., p. 377) that when compounds containing the benzene and thiophen nuclei are hydrogenised, the first addition of H_2 has a different thermal value to that of the second and third additions, which latter have the same value. The author noticed a similar difference in the case of pyrroline and its hydrogenised derivatives when the alterations of basicity are compared instead of the thermal values, thus:—pyrroline has very feeble basic properties, whilst its di- and tetrahydro-derivatives are strong bases. This, he believes, may be explained by assigning to pyrroline a centric formula in which the nitrogen exists in the pentavalent condition, and to the di- and tetrahydro-derivatives a mixed formula and an alicyclic formula respectively, containing trivalent nitrogen. The same applies to indole. The paucity of facts precludes for the present the extension of the discussion to other ring compounds containing five atoms—thiophen, furfuran, &c. A. R. L.

Hantzsch's Pyridine Synthesis. By C. BEYER (*Ber.*, **24**, 1662—1670).—The author brings forward a modified explanation of Hantzsch's pyridine synthesis, based on the results obtained by Claisen (*J. pr. Chem.* [2], **35**, 413; *Annalen*, **218**, 161), on the condensation of aldehydes with ethereal salts of ketonic acids. Claisen has stated that the group $\cdot CO\cdot CH_2\cdot CO\cdot$ attacks a double bond between two carbon atoms in such a way that one hydrogen atom of the methylene combines with one carbon atom, and the residue, $\cdot CO\cdot\dot{C}H\cdot CO\cdot$, with the other carbon atom. Thus ethyl malonate and ethyl ethylidenemalonate combine according to the equation $MeCH\!:\!C\cdot(COOEt)_2 + CH_2(COOEt)_2 = CHMe[CH(COOEt)_2]_2$. The author has studied Hantzsch's synthesis from the point of view indicated by the above reaction. He considers that in the presence of ammonia, aldehyde ammonia, or ethyl paramidoacetoacetate, the condensation takes place in the following stages:—First, the aldehyde condenses with the ethyl acetoacetate to form ethyl ethylidinacetoacetate, the latter then combines with a second molecule of the ethyl acetoacetate to form ethyl ethylidenediacetoacetate, and then the ammonia acts on the latter with formation of ethyl dihydrocollidinedicarboxylate. This is, however, contrary to the observation of Hantzsch, that ethyl benzylidenediacetoacetate, which has an analogous constitution to the above, does not yield a pyridine derivative with ammonia. It was therefore necessary to determine if a similar reaction took place between ethyl ethylidenacetoacetate and ethyl paramidoacetoacetate. If ethyl ethylidenacetoacetate is mixed in molecular proportion with ethyl paramidoacetoacetate, heat is evolved, a brisk reaction, with evolution of water, takes place, and almost pure ethyl dihydrocollidinedicarboxylate is obtained. The latter melts at 130°, and, when oxidised with nitrous acid, yields ethyl collidinedicarboxylate boiling at 308°. In a similar way, ethyl benzylidenacetoacetate and ethyl paramidoacetoacetate give ethyl dihydrophenyllutidinedicarboxylate. The intermediate additive compounds, which the author assumes are formed in the above reactions, cannot be separated.

The ammonia derivatives of benzoylacetone and of acetylacetone, corresponding with ethyl paramidoacetoacetate, were also examined in support of the above view. When benzoylacetonimide and ethyl ethylidenacetoacetate are warmed together in molecular proportion, a brisk reaction takes place, water is eliminated, and, on cooling, a yellow, crystalline mass of *ethyl 3-benzoyldihydrocollidinecarboxylate* is obtained. It crystallises from alcohol in yellow leaflets, melts at 186—187°, is an indifferent substance, dissolves, however, in concentrated mineral acids, but is precipitated unchanged on addition of water.

Ethyl 3-benzoylcollidinecarboxylate is obtained by oxidising the foregoing compound, suspended in alcohol, with nitrous acid. The product is washed with ether, the nitrate decomposed with potash, and the free base extracted with ether. It forms a viscid, pale-yellow liquid which partially decomposes on boiling, and so gives no constant boiling point. It dissolves easily in dilute hydrochloric or sulphuric acid, and double salts are obtained on adding picric acid or platinic chloride to the solution. The *hydrochloride* crystallises in prisms and melts at 192°. The *platinochloride* crystallises from dilute hydrochloric acid in needles.

The methylimide of benzoylacetone, $COPh\cdot CH_2\cdot CMe\colon NMe$, which is obtained by allowing a mixture of benzoylacetone and methylamine to remain some time, or by heating the mixture under pressure, and crystallises from light petroleum in beautiful leaflets melting at 74—75°, behaves in a similar way to benzoylacetonimide.

Ethyl methylbenzoyldihydrocollidinecarboxylate [$Me = 1$] is obtained by mixing the above methylimide with ethyl ethylideneacetoacetate; it crystallises from light petroleum in yellowish-white needles, and melts at 97°.

Ethyl 3-acetyldihydrocollidinecarboxylate is obtained in a similar way from acetylacetonimide. When the latter is mixed with ethyl ethylideneacetoacetate, a clear solution is obtained, heat is evolved, and on heating on the water-bath water is eliminated. Alcohol is then added, and the mixture cooled, when a crystalline mass is obtained. It crystallises from dilute methyl alcohol in flat, yellowish-white needles, melts at 120°, and resembles the analogous compounds described above. E. C. R.

Oxidation of Aniluvitonic Acid. By C. BÖTTINGER (*Annalen*, **263**, 247—248).—Doebner and Miller (Abstr., 1886, 721) found that quinaldine, on oxidation, yields acetanthranilic acid and oxalic acid, and that α-alkylcinchonic acids give only anthranilic acid derivatives. The author has previously shown (*Ber.*, **15**, 133) that aniluvitonic acid gives, on oxidation with potassium permanganate, the same pyridinetricarboxylic acid as is obtained from uvitonic acid under the same conditions; a repetition of these experiments, which seem to have been overlooked by Doebner and Miller, has confirmed the results previously published. F. S. K.

β-Picoline. By P. SCHWARZ (*Ber.*, **24**, 1676—1678).—β-Picoline is prepared by adding anhydrous glycerol (250 grams) to a mixture of phosphoric anhydride (200 grams) and dry ammonium phosphate (100 grams). The mixture is heated on the sand-bath in a reflux apparatus for about 50 hours, then diluted with water, and sodium hydroxide added to the well-cooled mixture. It is then distilled until the distillate reacts only faintly alkaline. The dilute solution of the base so obtained is mixed with solid soda and again distilled, when almost all the picoline is obtained in the first fractions, and is precipitated on addition of potash, and dried over potash. It boils at 140·5—143°, the greater part between 141—142°. When heated with benzaldehyde and a small quantity of zinc chloride at 230°, a small quantity of stilbazole, $C_{13}H_{11}N$, is obtained, identical with that obtained by Baurath from α-picoline (Abstr., 1888, 65, 608), and most of the β-picoline remains unchanged. Hence the author concludes that β-picoline prepared in the above way contains a small quantity of α-picoline, and that the former does not condense with benzaldehyde. All attempts to obtain a condensation product from β-picoline and benzaldehyde, or chloral, were unsuccessful.

The above results give a method of obtaining β-picoline free from α-picoline. β-Picoline, obtained as above, was converted into the mercurochloride, the latter recrystallised and decomposed. The β-picoline obtained boiled at 141·5—142°. It was heated with benzaldehyde and zinc chloride at 225—230°. A small quantity of stilbazole was obtained. The unattacked base was recovered and converted into the mercurochloride. The latter melts at 147—149°. The regenerated base boils at 141·5° (uncorr.; 143·5°, corr.), and has the sp. gr. 0·97256 at 0°/4°. The platinochloride melts at 201—202°, the aurochloride at 186°, and the picrate at 149—150°.

E. C. R.

Synthesis of Oxypyridine and Piperidine Bases. By A. LADENBURG (*Ber.*, **24**, 1619—1628; compare Abstr., 1890, 67).—α-Picolylalkine, $C_5NH_4·CH_2·CH_2·OH$, boils at 114—116° under a pressure of 9 mm. The *benzoyl derivative*, $C_5NH_4·CH_2·CH_2·OBz$, is a viscid liquid; the *platinochloride*, $(C_{14}NH_{13}O_2)_2,H_2PtCl_6$, crystallises from water and melts at 164—168°; the *aurochloride* is deposited in broad, lustrous prisms. Picolinic acid is the sole oxidation product of picrylalkine; no pyridylacetic acid could be detected.

The corrected boiling point of α-pipecolylalkine,

$$C_5NH_{10}\cdot CH_2\cdot CH_2\cdot OH,$$

is 234·5°. The *hydrochloride* and *mercurochloride* are both crystalline, and the former is very hygroscopic. The *benzoyl derivative* yields a *hydrochloride* which crystallises in small, colourless plates.

Methyl-α-pipecolylalkine, $C_5NH_9Me\cdot CH_2\cdot CH_2\cdot OH$, is prepared by heating α-pipecolylalkine with 5—6 parts of potassium methyl sulphate for 12—24 hours on the water-bath; the base is purified by means of the mercurochloride, and forms a colourless, viscid liquid boiling at 232·5° (corr.). The *platinochloride* is not crystalline; the *aurochloride* melts at 169—170°. The *mercurochloride*, $C_8NH_{18}OCl,5HgCl_2$, is deposited in well-developed crystals which melt at 214° without decomposition. On heating the base with methyl iodide in alcoholic solution, *methylpipecolylalkine methiodide*, $C_5NH_9Me\cdot CH_2\cdot CH_2\cdot OH,MeI$, is deposited in colourless prisms. The *hydrochloride* does not crystallise; the *platinochloride* melts at 173°; the *aurochloride* crystallises in lustrous, yellow needles, and melts at 211—212°. On treatment of the base with tropic acid and hydrochloric acid, a compound is obtained which affects the eyes in a similar manner to atropine; on this account, and from the general likeness of the other derivatives to those of tropine, the author regards the base as a dihydrotropine. All attempts hitherto made to prepare tropine by the oxidation of this hydrotropine have failed; on treatment with potassium ferricyanide at the ordinary temperature, a compound is obtained which is isomeric with tropine, and is therefore termed *paratropine;* it is a colourless, strongly alkaline liquid boiling at 200—203°, and readily dissolves in ether. The *hydrochloride* is crystalline and readily soluble; the *aurochloride*, $C_8NH_{15}O,HAuCl_4$, is deposited in small plates which melt at 181—182°; the *platinochloride* crystallises in transparent, orange-yellow prisms belonging to the monosymmetric system, and melts at 195—197° with decomposition. The *mercurochloride*, $C_8NH_{15}O,HCl,6HgCl_2$, is deposited from water in small crystals melting at 225° with decomposition.

By the action of hydriodic acid and phosphorus on paratropine at 150°, a compound is formed which crystallises from water in colourless needles, and is probably an iodide. J. B. T.

γ-Dipyridyl and γ-Dipiperidyl. By F. B. Ahrens (*Ber.*, **24**, 1478—1480).—The γ-dipiperidyl previously described by the author (Abstr., 1889, 59) is not a pure compound, but contains another substance which may be separated by converting the bases into their nitroso-compounds, that of γ-dipiperidyl being a solid and the other a liquid. γ-Dipyridyl is best prepared by allowing sodium to act on pyridine at the ordinary temperature in closed vessels until a homogeneous, black, pulverulent mass is obtained; this is exposed to the air until it becomes yellowish-white, then extracted with cold water, and the insoluble portion recrystallised from the hot liquid. It is reduced in amyl alcohol solution with a large excess of sodium, the solution acidified with concentrated hydrochloric acid, and the aqueous layer treated with sodium nitrite. On cooling, slender, yellowish needles separate, which are extracted with chloroform, the extract evaporated, and the residue recrystallised from alcohol. The *nitroso-γ-dipiperidyl* thus obtained forms yellow crystals and melts at 141—143°. The free *γ-dipiperidyl* is prepared from the nitroso-compound by dissolving it in concentrated hydrochloric acid, passing in hydrogen chloride, then adding freshly prepared soda solution, and extracting at once with ether. The extract is dried with potash and evaporated, the dipiperidyl being obtained in broad, transparent needles, which are hygroscopic, absorb carbonic anhydride from the air, and melt at about 160°. The *hydrochloride* crystallises in needles; the *platinochloride*, $C_{10}H_{20}N_2,H_2PtCl_6$, in very stable plates; and the *aurochloride*, $C_{10}H_{20}N_2,2HAuCl_4$, in long needles which gradually decompose when heated above 220°. The *mercurochloride* forms stellate aggregates of slender needles, is readily soluble in hot water, and melts with blackening at 226—227°. The *picrate* forms sparingly soluble, jagged plates and blackens when heated above 200°.

H. G. C.

Oxidation of Quinoline Derivatives. By W. v. MILLER (*Ber.*, **24**, 1900—1922; see also Abstr., 1890, 1324).—The results obtained by various observers show that when alkyl halogen additive compounds of quinoline are oxidised with permanganate, the pyridine ring is destroyed, and derivatives of orthoamidobenzoic acid are obtained. The pyridine ring is also destroyed in the case of carbostyril and cynurin, and generally in the case of hydrogen additive compounds. Both nuclei are destroyed in the oxidation of carbostyril methyl ether and methylpseudocarbostyril. The benzene nucleus is destroyed in aqueous or alkaline solution in the case of the following quinoline derivatives which contain substituents in the benzene nucleus:—Parabromoquinoline, parabromanaitroquinoline, ortho- and para-nitroquinoline, α- and β-dinitroquinoline, ortho- and para-hydroxyquinolinecarboxylic acids, orthohydroxydithioquinolinecarboxylic acid, orthoquinolinesulphonic acid, orthohydroxyquinoline, orthohydroxyparamidoquinoline, and α-hydroxyquinolinesulphonic acid. The benzene nucleus is destroyed in acid solution in the case of paramidophenylquinoline. Both the pyridine and benzene nuclei are destroyed on oxidation of γ-bromoquinoline in aqueous solution. Quinoline derivatives which contain substituents in both nuclei, generally undergo oxidation with destruction of the benzene ring.

From the above results, no general conclusion can be drawn unless it is assumed that the pyridine nucleus is destroyed in all cases where, according to v. Baeyer and Bamberger, the equality of the "central" or "potential" valence of the pyridine nucleus is destroyed, or where the pyridine nitrogen becomes pentavalent. The latter occurs in the oxidation of quinoline derivatives in acid solution; thus, on oxidation of aniluvitonic acid in alkaline solution, the benzene nucleus is destroyed, in acid solution the pyridine nucleus. In some other cases, where oxidation takes place with difficulty in alkaline liquids, it takes place easily in acid liquids. Paramidophenylquinoline is an exception, for in acid solution it yields α-hydroxynicotinic acid;

probably the presence of the amido-group has weakened the benzene nucleus.

When quinoline is oxidised in an aqueous solution with potassium permanganate, the benzene nucleus is destroyed, and pyridinedicarboxylic acid is obtained. Orthotoluquinoline and paratoluquinoline in like manner yield pyridinedicarboxylic acid.

The oxidation of methylquinolines, in which the methyl is in the pyridine nucleus, is influenced by the position of the methyl group. If the methyl group is in the γ-position, then the benzene nucleus is destroyed. If it is in the α-position, then the pyridine nucleus is destroyed. Substitution in the benzene nucleus does not appear to affect this rule. In the case of β-methylquinoline, both nuclei are destroyed, and oxalic acid, carbonic anhydride, and ammonia are formed. If, besides methyl in the α position, a second methyl group is present, then if the second methyl group is next the α-methyl, the pyridine nucleus is destroyed; if the second methyl group is in the γ-position, the benzene nucleus is destroyed.

If the pyridine nucleus contains carboxyl, then the benzene nucleus is always destroyed, and a pyridinecarboxylic acid is formed.

Orthotoluquinaldine.—The base (10 grams) is suspended in 1½ litres of water and permanganate (42 grams) dissolved in water (500 c.c.) gradually added; the mixture is made neutral or faintly acid with sulphuric acid, and heated for 1—2 hours on the water-bath. The filtered solution is evaporated to dryness, and the product extracted with absolute alcohol; the alcoholic solution deposits a mixture of the acid and its potassium salt; it is dissolved in soda, and the acid precipitated with hydrochloric acid; it was identified as *acetylamidotoluic acid*. It crystallises from water or alcohol in shining, prismatic needles, melts at 193—194°, and is easily soluble in hot water and alcohol, sparingly in ether, and insoluble in dilute mineral acids; in concentrated mineral acids it dissolves with decomposition. The *silver* salt forms white needles, and quickly darkens on exposure to light. The *calcium* salt forms white, shining plates.

If the acid is heated above 200°, or if it is distilled with baryta, carbonic anhydride is split off, and orthotoluidine is obtained.

α-β-Dimethylparatoluquinoline was oxidised as described by Doebner and v. Miller for quinaldine; the acid obtained gave numbers corresponding with *methylacetanthranilic acid;* it crystallised from alcohol and water in white, asbestos-like needles, and melted at 193—194°.

Ethylquinoline [Et = 2′], when oxidised in alkaline solution, gives very bad results. In acid solution, however, oxidation takes place easily in the cold. The base is dissolved in dilute sulphuric acid, gradually mixed with a solution of permanganate, and the mixture kept acid by constant additions of sulphuric acid. The acid obtained was identified as propionylorthamidobenzoic acid. It crystallises best from high boiling petroleum in white, lustrous needles, and melts at 117°.

Methylquinoline [Me = 3′] is best prepared by saturating a mixture of formaldehyde (40 per cent., 100 grams) and propaldehyde (85 grams) with dry hydrogen chloride, adding to a mixture of aniline (120 grams) and concentrated hydrochloric acid (240 grams), and heating in a reflux apparatus for some hours on the water-bath. The oxidation gave very bad results. The base (10 grams) was suspended in 5 per cent. caustic potash (1500 grams), and heated in a reflux apparatus on the water-bath. The products were ammonia, carbonic anhydride, oxalic acid, the oxalate of the base, a brown, resinous mass, and some quantity of the base which remained unchanged.

Dimethylquinoline [$Me_2 = 2' : 4'$] is purified by conversion into the picrate, decomposing the latter with soda, distilling with steam, and finally by fractional distillation. It boils at 260—261°. For the oxidation, the base (10 grams) is suspended in 7 per cent. potassium carbonate solution (1500 c.c.), 4 per cent. permanganate solution gradually added, and the mixture heated on the water-bath. The product contains a condsiderable quantity of oxalic acid; it was neutralised, converted into the silver salt, then into the barium salt; the latter decomposed, and the acid crystallised from absolute alcohol. It was identified as picolinetricarboxylic acid; it crystallises in white, fibrous crusts, turns yellow at 189°, begins to sublime at 210°, turns brown at 210—230°, and melts at 235° with frothing and evolution of carbonic anhydride. Together with the above acid, a small quantity of the tetracarboxylic acid is formed. The same result is obtained by oxidation in the cold.

Quinaldinic acid is best prepared by oxidising benzylidenequinaldine with chromic acid. Benzylidenequinaldine is prepared by heating quinaldine (115 grams) with benzaldehyde (90 grams) for 4—5 hours in a sulphuric acid bath at 140—150°, and adding zinc chloride to the mixture from time to time until the further addition of zinc chloride causes no reaction. The mixture is then poured into a basin, and the crystalline mass extracted with concentrated hydrochloric acid and hot water; the filtered solution, on cooling, deposits crystals of benzylidenequinaldine hydrochloride. The latter was filtered off and decomposed with ammonia, and the benzylidenequinaldine dried on porcelain plates and crystallised from alcohol. It crystallises in colourless needles, melts at 99—100°, is insoluble in water, and easily soluble in chloroform and carbon bisulphide. The benzylidenequinaldine (10 grams) is dissolved in dilute sulphuric acid (200 c.c.), the solution gently boiled, and chromic acid (15 grams) in water (70 grams) and concentrated sulphuric acid (75 grams) gradually added. When the mixture has cooled somewhat, $\frac{3}{4}$ litre of water is added, and the mixture allowed to stand 48 hours. The solution is freed from benzoic acid by extraction with ether; the chromium precipitated with ammonia, filtered hot, and the filtrate evaporated to dryness and extracted with alcohol. The quinaldinic acid crystallises from water in asbestos-like needles, and melts at 156°.

The oxidation is carried out as follows:—The quinaldinic acid (10 grams) is dissolved in water (500 grams) containing a slight excess of potassium carbonate, and the cold solution gradually mixed with a cold saturated solution of permanganate (41 grams), and allowed to remain for a few days. It is then heated on the water-bath, filtered, and the filtrate acidified with sulphuric acid, and dilute permanganate added as long as it is at once decolorised. The solution is then neutralised with ammonia and concentrated on the water-bath, again acidified with sulphuric acid, and the sulphate precipitated with alcohol; after being treated in this way once or twice to get rid of all the sulphate, the filtrate is concentrated and allowed to crystallise. After some days, a crystalline crust of pyridinetricarboxylic acid $[(COOH)_3 = 2:5:6]$ is obtained. It is purified by conversion into the calcium salt, decomposing with sulphuric acid, converting into silver salt, and decomposing with hydrogen sulphide. It crystallises from water in thin leaflets, gives off carbonic anhydride at 130°, melts at 236—237°, and decomposes again above 237°, and is easily soluble in dilute alcohol and water, almost insoluble in ether, absolute alcohol, and acetic acid. The solution neutralised with ammonia gives white, insoluble precipitates with barium chloride, calcium chloride, lead nitrate, and silver nitrate; an olive-green precipitate with copper acetate, a yellowish-white with ferric chloride, and a carmine-red with ferrous sulphate.

α-Methylcinchoninic acid is obtained by gradually adding aniline (1 mol.) to a mixture of acetylcarboxylic acid (1 mol.) and acetaldehyde (1 mol.) diluted with absolute alcohol, and heating the mixture for 4—5 hours in a reflux apparatus on the water-bath.

For oxidation in alkaline solution, the acid (10 grams) is dissolved in warm water containing a slight excess of potassium carbonate, permanganate (56 grams in $1\frac{1}{2}$ litres of water) added, and the mixture warmed. The solution contained oxalic acid and an acid which, on analysis, gave numbers corresponding with picolinetricarboxylic acid. The latter was extremely difficult to purify, is easily soluble in water, insoluble in alcohol and ether, and decomposes at 210—220°. With iron sulphate it gives a red coloration.

In acid solution, the oxidation takes place in the cold, and acetylanthranilic acid (m. p. 179—180°) is obtained. E. C. R.

Alicyclic Homology. By E. BAMBERGER (*Ber.*, **24**, 1897—1899).—In accordance with the views lately put forward by the author, dihydroindole and tetrahydroquinoline, although derived from distinctly different mother substances, ought both to behave like alkylated anilines. Dihydroindole itself is not known; the author has, therefore, compared the homologous dihydromethylketole with tetrahydroquinoline. These two bases are related to each other in the same way as propylaniline to isopropylaniline. The author finds that they behave alike. Thus hydromethylketole, when treated with a diazo-compound in the presence of sodium acetate, like hydroquinoline, yields a diazoamido-compound which crystallises in beautiful columns. In the presence of mineral acids, the reaction also takes place as with hydroquinoline, and the azo-group enters the benzene nucleus in the para-position. The azo-dye so obtained closely resembles the corresponding hydroquinoline dye, yields, on reduction, a diamine which gives the same characteristic colour reaction as paramidotetrahydroquinoline, and, like the latter, behaves as an alkylparaphenylenediamine. E. C. R.

Methoxydihydroxydihydroquinoline. By A. EICHENGRÜN and A. EINHORN (*Annalen*, **262**, 133—181).—*Metachlorobenzaldehydephenylhydrazone*, $C_6H_4Cl·CH:N_2HPh$, crystallises from alcohol in colourless needles, melts at 134—135°, and is readily soluble in alcohol, ether, ethyl acetate, and chloroform, but more sparingly in light petroleum: its alcoholic solution decomposes on keeping.

Orthonitrometachlorobenzaldehyde, $NO_2·C_6H_3Cl·CHO$, is obtained when metachlorobenzaldehyde (compare Erdmann and Schwechten, this vol., p. 448) is added drop by drop to a well-cooled mixture of concentrated sulphuric acid and potassium nitrate; it crystallises from alcohol in lustrous needles, melts at 77·5°, is readily soluble in hot water and most ordinary solvents, and is volatile with steam. On oxidation with potassium permanganate, it is converted into metachloronitrobenzoic acid (m. p. 137°). The *hydrazone*, $C_{13}H_{10}N_3O_2Cl$, crystallises from alcohol in needles, melts at 180—181° with decomposition, and is soluble in alcohol, ether, glacial acetic acid, chloroform, and benzene, but insoluble in light petroleum. The *oxime*, $C_7H_5N_2O_3Cl$, crystallises from alcohol in colourless, prismatic plates, and from hot water in needles, melts at 112°, and is readily soluble in the ordinary solvents.

Orthonitrometachlorophenyllactic ketone,

$$CO[CH_2·CH(OH)·C_6H_3Cl·NO_2]_2,$$

is formed in small quantities (1—2 per cent.), together with a small quantity (2—3 per cent.) of orthonitrometachlorocinnamic ketone by the condensation of pure acetone with orthonitrometachlorobenzaldehyde at 0° in presence of dilute soda, but the principal product of the reaction is orthonitrometachlorophenyllactic methyl ketone (compare Abstr., 1890, 1128); the three products are separated by taking advantage of their different solubilities in alcohol. Orthonitrometachlorophenyllactic ketone separates from ethyl acetate in lustrous, dendritic forms, melts at 207·5—208·5° with decomposition, and is readily soluble in benzene, ethyl acetate, glacial acetic acid, and hot alcohol, but only sparingly in chloroform and ether, and insoluble in light petroleum; on prolonged boiling with concentrated soda, it yields small quantities of dichlorindigo. The *hydrazone*, $C_{23}H_{20}O_6N_4Cl_2$, crystallises from glacial acetic acid in small, deep red needles, melts at 193·5°, and is readily soluble in most ordinary solvents, except light petroleum.

Orthonitrometachlorocinnamic ketone, $CO(CH:CH·C_6H_3Cl·NO_2)_2$ (see above), is also formed when the preceding compound is boiled with acetic anhydride; it crystallises in golden needles, melts at 205—206°, and is soluble in hot benzene, glacial acetic acid, and ethyl acetate, but more sparingly in chloroform, and insoluble in alcohol, ether, and light petroleum. The *tetrabromide*, $C_{17}H_{10}O_5Cl_2N_2Br_4$, prepared by treating the ketone with bromine in glacial acetic acid solution, crystallises in colourless, lustrous needles, melts at 199—200° with decomposition, and is soluble in chloroform, benzene, and glacial acetic acid. The *hydrazone*, $C_{23}H_{16}N_4O_4Cl_2$, crystallises from glacial acetic acid in slender, carmine-red needles, melts at 194—195° with decomposition, and is readily soluble in hot glacial acetic acid, ethyl acetate, and chloroform, but insoluble in alcohol, ether, and light petroleum.

Orthnitrometachlorophenyllactic methyl ketone,

$$NO_2\cdot C_6H_3Cl\cdot CH(OH)\cdot CH_2\cdot COMe$$

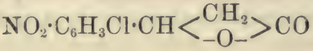
(*loc. cit.*), crystallises in colourless, hexagonal plates, $a : b : c = 0{\cdot}6412 : 1 : 1{\cdot}4375$, $\beta = 76° 4'$, belonging to the monoclinic system; it dissolves in concentrated sulphuric acid with a red coloration, and is immediately converted into dichlorindigo by alkalis. The *hydrazone*, $C_{16}H_{16}N_3O_3Cl$, crystallises from glacial acetic acid in wine-red needles, melts at 157—158°, and is soluble in most ordinary solvents, except light petroleum. The *oxime*, $C_{10}H_{11}N_2O_4Cl$, separates from alcohol in small plates, melts at 151°, and is soluble in ethyl acetate, but only sparingly soluble in benzene, chloroform, and light petroleum, and insoluble in ether.

Orthonitrometachlorobenzylideneacetone, $NO_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot COMe$, is formed when the preceding compound is boiled with acetic anhydride; it crystallises from alcohol in colourless prisms, melts at 143°, and is soluble in glacial acetic acid, ethyl acetate, benzene, and chloroform, but more sparingly in ether and light petroleum. The *hydrazone*, $C_{16}H_{14}N_3O_2Cl$, crystallises from glacial acetic acid in slender needles, melts at 161°, and dissolves in glacial acetic acid, alcohol, and ethyl acetate with a red, and in ether, benzene, chloroform, and light petroleum with a yellow, coloration.

Orthonitrometachlorophenyl-β-lactic acid (*loc. cit.*) forms monoclinic crystals, $a : b : c = 0{\cdot}8652 : 1 : 1{\cdot}8184$, $\beta = 78° 40'$ (m. p. 156° with decomposition), and is readily soluble in alcohol, ether, chloroform, benzene, acetone, ethyl acetate, and glacial acetic acid, but more sparingly in hot water, and insoluble in light petroleum; it dissolves in concentrated sulphuric acid with a red coloration, and, when heated with potash, it gives off an odour of nitrobenzene, yielding a red solution which becomes colourless on cooling. The *potassium* salt, $C_9H_7NO_5ClK$, crystallises from dilute alcohol in colourless, lustrous needles, turns brown on exposure to light, and is very readily soluble in water and ethyl acetate, but insoluble in absolute alcohol; the barium, calcium, silver, and copper salts are crystalline. The *ethyl* salt, $C_{11}H_{12}ClNO_5$, forms small, nodular crystals, melts at 110°, and is readily soluble in all ordinary solvents, except water. When the potassium salt of the acid is heated at 100° with a methyl alcoholic solution of potassium methoxide, a small quantity of an acid, probably methoxynitrophenyl actic acid, which melts at 125—126°, is obtained.

Orthonitrometachlorocinnamic acid, $NO_2\cdot C_6H_3Cl\cdot CH{:}CH\cdot COOH$, prepared by heating orthonitrometachlorobenzaldehyde with acetic anhydride and sodium acetate, crystallises from dilute alcohol in colourless needles, melts at 174—175°, turns reddish on exposure to light, and is readily soluble in glacial acetic acid, ethyl acetate, acetone, and chloroform, but only sparingly in benzene, and almost insoluble in light petroleum; it dissolves in concentrated sulphuric acid with a green coloration. The *silver* salt, $C_9H_5NO_4ClAg$, crystallises from dilute alcohol in colourless needles, and is soluble in hot water. The *barium* salt, $(C_9H_5NO_4Cl)_2Ba + 3H_2O$, *calcium* salt $(+1\frac{1}{2}H_2O)$ and the *copper* salt ($+1\frac{1}{2}H_2O$) are crystalline. The *ethyl* salt, $C_{11}H_{10}NO_4Cl$, crystallises from alcohol in long, colourless needles, melts at 62°, and is very readily soluble in all ordinary solvents, except water, in which it is insoluble.

Orthonitrometachlorophenyl-β-lactic acid (m. p. 152°), prepared as previously described (*loc. cit.*) from the lactone,



$$\mathrm{NO_2\cdot C_6H_3Cl\cdot CH}{<}\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{-\mathrm{O}-}{>}\mathrm{CO}$$

(m. p. 147° with decomposition), or from the lactamide,

$$\mathrm{NO_2\cdot C_6H_3Cl\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH_2}$$

(m. p. 148°), is very readily soluble in alcohol, chloroform, ethyl acetate, and light petroleum, but rather more sparingly in ether, benzene, and warm water, and insoluble in light petroleum; it dissolves in sulphuric acid, yielding a bluish-green solution. The calcium salt and the salts of the alkalis are soluble in water, but the barium, copper, and lead salts are insoluble; the silver salt crystallises from ammonia in colourless needles, is soluble in hot water, and rapidly darkens on exposure to light. The *ethyl* salt, $C_{11}H_{12}ClNO_5$, crystallises from light petroleum in colourless, hexagonal plates, melts at 48°, and is readily soluble in alcohol, ether, ethyl acetate, benzene, and chloroform, but only sparingly in light petroleum.

A comparison of the properties of the two orthonitrometachlorophenyl-β-lactic acids (m. p. 152° and 156° respectively) and of those of their derivatives shows, beyond doubt, that the two acids are not identical.

Chlorodihydroxydihydroquinoline [$H_2:(OH)_2:Cl = 3':4':2':4':3$], prepared by reducing orthonitrometachlorophenylactic acid (m. p. 152°) with ferrous sulphate and ammonia, crystallises from ethyl acetate in slender needles, melts at 172°, and is readily soluble in alcohol and warm water, but more sparingly in chloroform, benzene, and ether, and insoluble in light petroleum; when its aqueous solution is warmed with ferric chloride, there is produced a bright red coloration which disappears on cooling, and, when boiled with water, it is converted into chlorocarbostyril (m. p. 262—263°), identical with the compound prepared by Einhorn and Lauch from parachloroquinoline.

Orthonitrometachlorophenyl-β-lactaldehyde,

$$\mathrm{NO_2\cdot C_6H_3Cl\cdot CH(OH)\cdot CH_2\cdot CHO}$$

(*loc. cit.*), is a colourless oil, readily soluble in most ordinary solvents, except light petroleum; its *hydrazone*, $C_{15}H_{14}N_3O_3Cl$, crystallises in long, orange-red needles, melts at 182°, and is readily soluble in benzene and chloroform, but more sparingly in alcohol and glacial acetic acid, and very sparingly in ether and light petroleum.

Orthonitrometamethoxyphenyllactic acid (m. p. 106°) is readily soluble in warm water, alcohol, chloroform, and ethyl acetate, but more sparingly in ether, and very sparingly in light petroleum and benzene; when heated with concentrated sulphuric acid, it gives a green solution, the colour of which changes first to violet, and then to a brownish-red on boiling. The potassium salt crystallises from hot water in lustrous plates; the calcium salt is readily soluble in water, but the barium salt and the lead salt are insoluble.

Orthonitrometamethoxycinnamic acid (m. p. 224·5—225·5°) is soluble in glacial acetic acid and ethyl acetate, but only sparingly soluble in benzene, ether, and chloroform, and almost insoluble in light petroleum. The *silver* salt, $C_{10}H_8NO_5Ag + \frac{1}{2}H_2O$, crystallises from dilute alcohol in colourless needles, quickly turns brown on exposure to light, and is readily soluble in alcohol and ammonia, but only sparingly in hot water. The *calcium* salt, $(C_{10}H_8NO_5)_2Ca + 2H_2O$, crystallises from dilute alcohol in colourless needles, and is insoluble in water; the *barium* salt and the dark blue *copper* salt ($+2H_2O$) are crystalline. The *ethyl* salt, $C_{12}H_{13}NO_5$, is readily soluble in alcohol and ethyl acetate, but more sparingly in benzene and chloroform, and very sparingly in ether and light petroleum; it crystallises from alcohol in long needles melting at 72·5°.

Paramethoxydihydroxydihydroquinoline (*loc. cit.*), prepared from orthonitrometamethoxyphenyllactic acid, crystallises from cold water in colourless needles, melts at 177°, and is readily soluble in alcohol, ethyl acetate, and warm water, but only sparingly in chloroform and benzene, and almost insoluble in ether and light petroleum; when warmed with ferric chloride in aqueous solution, it gives a blood-red coloration, which changes to a brownish-red at a higher temperature.

Paramethoxycarbostyril [OH : OMe = 2′ : 3] separates from ethyl acetate in yellow or brown, rhombic crystals ($a : b : c = 0·8280 : 1 : 0·3866$), melts at 218—219°, and is readily soluble in alcohol, chloroform, and ethyl acetate, but only sparingly in benzene and water, and insoluble in ether and light petroleum. F. S. K.

Synthesis of Quinaldine. By W. v. Miller (*Ber.*, **24**, 1720—1728).—The author gives in detail the various hypotheses which have been advanced to explain the mechanism of the formation of quinoline derivatives when aniline is heated with certain aldehydic compounds in the presence of hydrochloric acid. The assumption that the initial interaction takes place between the aldehydic oxygen and the hydrogen atom in the ortho-position to the amido-group of aniline, a side chain being introduced which subsequently forms a closed ring, appears at first sight plausible, and is in accordance with the view that the methyl group in quinaldine occupies the position 2′; it seems specially to apply to those cases in which the formation of a quinoline derivative is possible; for in cases in which it is not possible, the aldehyde residue takes up the para-position to the amido-group, as instanced in the formation of a triphenylmethane derivative from aniline and benzaldehyde. This hypothesis fails, however, to explain the fact that the yield of 2′-phenylquinoline, by heating cinnamic anilide with hydrochloric acid, is not improved by the presence of cinnamaldehyde. It is well known that alkyl derivatives of aniline are formed as bye-products in the synthesis of quinoline derivatives; and it seems feasible that when aniline, aldehyde, and hydrochloric acid are heated together, ethylidene aniline is first produced, and that this interacts with another molecule of aldehyde, giving rise to the compound NPh:CH·CH:CHMe.

This could not be put to the test, as, according to Tollens (*Ber.*, **17**, 659), ethylideneaniline cannot be prepared. When, however, valerylideneaniline (Lippmann and Strecker, Abstr., 1879, 462) is mixed with valeraldehyde in molecular proportion, and hydrochloric acid added, a violent reaction ensues, and, after boiling the mixture for several hours, a good yield of 2′-isobutyl-3′-isopropylquinoline (Spady, Abstr., 1886, 263) is obtained. When the order of the reagents is altered, or when valerylideneaniline is heated with hydrochloric acid alone, the yield of the quinoline derivative is greatly diminished. The author is of opinion, therefore, that the intermediate compound $CHMe_2{\cdot}CH_2{\cdot}CH{:}C(CHMe_2)CH{:}NPh$ is initially formed, which then undergoes isomeric change into isobutylisopropylquinoline. The same result is obtained when valerylideneaniline is fused with anhydrous zinc chloride. When toluidopyruvic acid,

$$C_6H_4Me{\cdot}N{:}CMe{\cdot}COOH,$$

is fused with zinc chloride, a considerable yield of toluquinaldine and paramethyl-α-cinchoninic acid is obtained. Schultz (*Ber.*, **16**, 2600) found that the initial product of the action of aldehyde on aniline was the compound $NPh{:}CH{\cdot}CH{:}CHMe,NH_2Ph$; assuming that aniline is split off when this is fused with zinc chloride, crotonylideneaniline, $NPh{:}CH{\cdot}CH{:}CHMe$, would be the intermediate compound in this instance. When the side-chains of these intermediate bases form a closed ring, dihydroquinoline derivatives might be expected to be formed, and this finds confirmation in the investigation of aldehyde-green (compare v. Miller and Plöchl, this vol., p. 1070). In the case of dihydroquinaldine, however, this is so unstable that a portion is oxidised to quinaldine, whilst another portion is converted into tetrahydroquinaldine. A. R. L.

Colouring Matters from Hydroquinaldine. By W. v. MILLER and J. PLÖCHL (*Ber.*, **24**, 1715—1720).—Tetrahydroquinaldine is purified by means of the acetyl derivative. When tetrahydroquinaldine (17 grams) and paranitrobenzaldehyde (8 grams) are dissolved in absolute alcohol and heated on the water-bath for two hours with zinc chloride (20 grams), and the residue, after removing the zinc with a concentrated solution of sodium hydroxide, is collected, washed, dried, and dissolved in hot alcoholic hydrochloric acid, yellow flocks separate on cooling. The base obtained by treating the latter with ammonia is amorphous, and dissolves readily in benzene, alcohol, and ether; on adding petroleum to its solution in benzene, yellow, amorphous flocks separate; but the substance was not obtained in the pure state. On treating it with chloranil in alcoholic solution, a green dye is formed.

Amidophenylditetrahydroquinaldylmethane, $C_{27}H_{31}N_3$, is formed when the last-described base is reduced with tin and hydrochloric acid. After removing the tin by a current of hydrogen sulphide, the base is precipitated by ammonia; it is dissolved in alcohol and evaporated, redissolved in hydrochloric acid, and again precipitated by ammonia; it is then repeatedly dissolved in benzene and reprecipitated by light petroleum. It is a colourless, amorphous substance, soluble in alcohol, ether, and benzene, but insoluble in petroleum and water, and yields a reddish-violet dye on treatment with chloranil in alcoholic solution. Solutions of its salts give amorphous precipitates with platinic or mercuric chlorides. The *monobenzoyl derivative*, $C_{34}H_{35}N_3O$, is prepared by shaking a solution of the base in benzene with benzoic chloride and sodium hydroxide; it forms small, silky, nodular aggregates of crystals.

Conversion of the Amido-compound into the Quinaldine Derivative.—The amido-compound (40 grams) is dissolved in concentrated hydrochloric acid (100 grams) and heated on the water-bath; aldehyde (25 grams) is gradually added and the heating continued for three hours; it is well diluted and treated with hydrogen sulphide and sulphurous anhydride, when resinous substances are precipitated; after removing these, ammonia precipitates the leuco-base as a brownish, amorphous compound which is readily soluble in alcohol, less in benzene and ether, and still less in light petroleum. It yields a bluish-green dye on oxidation with chloranil.

Tritetrahydroquinaldylmethane, $CH[C_9NH_9Me]_3$, is formed when the last-mentioned crude leuco-base is heated on the water-bath with tin and hydrochloric acid. A certain quantity of the hydrogenation product is extracted, after the addition of sodium hydroxide to the solution, by ether, whilst the main quantity is obtained from the stannochloride which separates out; the latter is repeatedly heated with sodium hydroxide, the dried cake extracted with ether, and the ethereal solution filtered and evaporated. The residue is dissolved in dilute hydrochloric acid, and after adding water and filtering, the base is precipitated with ammonia; it is then dissolved in benzene, and the resinous substances precipitated by adding light petroleum; the base then separates after a while in almost white flocks. It is soluble in alcohol, ether, and benzene; its solution in benzene, when not too concentrated, is not precipitated by light petroleum. A beautiful, bluish-violet dye is obtained on oxidation with chloranil in ethereal solution, which is converted into a green dye by heating with methyl iodide, but not by hydrogen sulphide and sulphurous anhydride; hydrochloric acid also determines the change from blue to green, but in this case the blue is reproduced by diluting with water; its analogy to methyl-violet is therefore unmistakable. A. R. L.

Fluorescent Derivatives of Aromatic Diamines. By W. v. Miller (*Ber.*, **24**, 1729—1745; compare Schiff and Vanni, *Annalen*, **253**, 319; Abstr., 1890, 139).—The results described below are altogether at variance with those of Schiff and Vanni (*loc. cit.*). When metaphenylenediamine hydrochloride (15 grams) is dissolved in about 1 litre of alcohol and heated on the water-bath for 1½ hour with œnanthaldehyde (35 grams), a green, fluorescent solution is obtained, and on adding an alcoholic solution of picric acid and some ether, the picrate separates after a time, together with much brown oil; it is crystallised from glacial acetic acid, and the crystals treated with ammonia, the resulting brown oil being extracted with ether. A brown, crystalline mass is obtained on evaporating the ethereal solution, which, on repeated crystallisation from alcohol, forms, on drying, white, felt-like needles of the composition $C_{34}H_{52}N_2$. The pure *base* is readily soluble in most solvents, but sparingly in alcohol; its alcoholic solution does not exhibit fluorescence, and the latter property in solutions of the crude base appears to be due to the presence of a hydrogenised derivative; it melts at 50—51°. The *hydrochloride* dissociates when heated with water. The *platinochloride*,

$$C_{34}H_{52}N_2,H_2PtCl_6 + 2H_2O,$$

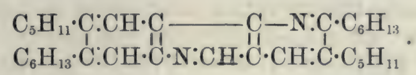
is obtained when concentrated hydrochloric acid and platinic chloride is added to an alcoholic solution of the base, and the precipitated compound crystallised from alcohol containing hydrochloric acid and platinic chloride; it forms an orange-yellow, crystalline powder, and melts at 201—210° with decomposition. The composition of the latter compound is, according to Schiff and Vanni, $2C_{19}H_{32}N_2,H_2PtCl_6$. The *picrate* crystallises from alcohol in small, bright-yellow, felt-like needles, and melts at 104°. The base is a *diamyldihexylphenanthroline*, and its constitution is proved by the following experiments:—

Nitroamylhexylquinoline,

$$NO_2\cdot C_9NH_4(C_6H_{13})\cdot C_5H_{11}\ [NO_2 : C_6H_{13} : C_5H_{11} = 4 : 2' : 3'],$$

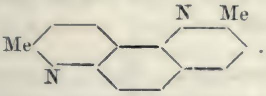
is prepared by heating metanitraniline (15 grams) dissolved in alcohol (500 c.c.) on the water-bath with œnanthaldehyde (20 grams) for $1\frac{1}{2}$ hour. The solution of the crude substance exhibits a faint-green fluorescence, and the base is purified by converting it into the picrate and crystallising the latter from glacial acetic acid, decomposing with ammonia, and extracting with ether; on repeatedly crystallising from alcohol, it forms small, white, felt-like needles, dissolves readily in benzene, chloroform, and carbon bisulphide, but less easily in ether, petroleum, acetone, and alcohol; it is insoluble in dilute acids, and melts at 53°. The *platinochloride* crystallises from alcohol in reddish-yellow needles; the *picrate* separates from alcohol in glittering, friable plates, and melts at 153°.

The *amido-derivative*, $C_{20}H_{30}N_2$, is obtained when the nitro-compound (10 grams) is dissolved in alcohol and heated on the water-bath for an hour with stannous chloride (25 grams) and hydrochloric acid; the solution is poured into a hot, concentrated solution of sodium hydroxide, and, after diluting with water, extracted with ether; on distilling off the latter, a red oil is obtained, which solidifies to a reddish-brown mass and dissolves in alcohol with a green fluorescence. It is crystallised from petroleum, and forms a white, felt-like mass of crystals which change to red in the air, especially in the moist condition; it is readily soluble in alcohol, ether, benzene, and chloroform, sparingly in petroleum, and melts at 68—69. The *picrate* crystallises from alcohol in long, yellow, woolly needles, sinters at 180°, and melts at 194° with decomposition. The *platinochloride* separates from alcohol containing platinic chloride and hydrochloric acid in small, dense, orange-yellow plates containing 4 mols. H_2O which effloresce in the air. When the amido-derivative (20 grams) is dissolved in 1 litre of water and heated on the water-bath for an hour with œnanthaldehyde (20 grams), a dark-red solution having a green fluorescence is obtained; sodium nitrite (10 grams) is then added to decompose the unaltered amido-derivative, and the base isolated by means of the picrate; it is identical with the above-described diamyldihexylphenanthroline, and has the following constitution:—



$$\begin{array}{l} C_5H_{11}\cdot C{:}CH\cdot C\text{———}C{-}N{:}C\cdot C_6H_{13} \\ C_6H_{13}\cdot C{:}CH\cdot C\cdot N{:}CH\cdot C\cdot CH{:}C\cdot C_5H_{11} \end{array}.$$

Dimethylphenanthroline, $C_{14}H_{12}N_2$, is prepared by heating metaphenylenediamine hydrochloride (25 grams) and concentrated hydrochloric acid (75 grams) at 110° in a sulphuric acid bath, with the gradual addition of paraldehyde (60 grams); the temperature is then raised to 150—160°, and the mixture maintained at this for four hours; it is then diluted with water (2 litres), filtered, and boiled with sodium nitrite; on again filtering the solution, it exhibits a green fluorescence when diluted with water. Sodium hydroxide is added, and the precipitate collected and dried, both the latter and filtrate being then extracted with ether; on distillation, the base passes over above 360° as a yellow oil which solidifies to a transparent cake; the yield is 16 grams. It is purified by dissolving in dilute hydrochloric acid and nearly neutralising with ammonia; the dark-brown substance which precipitates is then quickly filtered off, an excess of ammonia added to the filtrate, and the crystalline, hydrated base, which separates after a time, collected; it melts at 76—78°, and forms long, colourless, anhydrous needles on crystallisation from light petroleum, and then melts at 97—98°. It is readily soluble in most organic solvents, and in dilute acids, but sparingly soluble in cold light petroleum and water, more readily in a hot aqueous solution of ammonia. Solutions of the pure base do not exhibit fluorescence; it is not very volatile with steam. When heated with tin and hydrochloric acid on the water-bath for five hours, the resulting solution exhibits no fluorescence. It is rendered alkaline by sodium hydroxide and extracted with benzene; the benzene solution is then shaken with benzoic chloride and 10 per cent. sodium hydroxide for 10 hours, and after separating from the aqueous portion, repeatedly extracted with very dilute hydrochloric acid, from which, on neutralisation with ammonia, the *monobenzoyl derivative* of the *octohydro-base* separates. It is crystallised once from dilute alcohol, and twice from a mixture of light petroleum and benzene, and melts at 167—168°; it forms a solid *nitroso-derivative*. From the above benzene solution, extracted with dilute hydrochloric acid, a second compound is obtained as a viscid mass which does not solidify when kept over sulphuric acid. When metaphenylenediamine hydrochloride is dissolved in alcohol and heated on the water-bath for four hours with twice its weight of aldehyde, a small yield of the dimethylphenanthroline is formed, and the latter is likewise obtained by the condensation of metamidoquinaldine with aldol, or with paraldehyde; it must therefore have the constitution



A. R. L.

Triquinylmethane. By E. NOELTING and C. SCHWARTZ (*Ber.*, **24**, 1606—1609).—The authors call the group C_9NH_6 quinyl.

Triquinylmethane, $CH(C_9NH_6)_3$, is obtained by heating a mixture of pararosaniline (22 grams), glycerol (64 grams), sulphuric acid (52 grams), and picric acid (7 grams) for 3—4 hours at 140—150°. The cold melt is poured into water, carefully neutralised with soda, and the brown precipitate dried and extracted with benzene. The benzene solution is shaken with dilute sulphuric acid, and the base reprecipitated with ammonia in ice-cold solution. It is obtained as a greenish powder, which is dissolved in benzene, and petroleum added as long as resinous compounds are precipitated; the solution is then filtered and allowed to crystallise in a vacuum over paraffin and sulphuric acid. It crystallises in white needles and melts at 202°; from alcohol it crystallises in plates, melts at 97—98° with loss of water, or alcohol, of crystallisation, solidifies at a higher temperature, and melts finally at 202°. It is easily soluble in alcohol, benzene, and ether, sparingly in light petroleum, carbon bisulphide, and boiling water, and gives no coloration with chloranil and lead peroxide in acetic acid solution. The salts are easily soluble, with the exception of the picrate and platinochloride. The *trihydrochloride* is obtained by leading hydrogen chloride into a solution of the base in benzene; it crystallises in white plates, is soluble in water and alcohol, and insoluble in benzene and absolute ether. The *picrate* is obtained by mixing alcoholic solutions of triquinylmethane and picric acid, and crystallises from dilute alcohol in slender, yellow needles. The *platinochloride*, $4C_{28}H_{22}N_3Cl_3,3PtCl_4 + 3H_2O$, is obtained in yellow crystals; it is sparingly soluble in cold water, more easily in hot water and alcohol, and crystallises with 3 mols. H_2O, which it loses at 120°. The *methiodide*, $CH(C_9NH_6MeI)_3$, is obtained by heating the base with excess of methyl iodide at 105° for three hours. It crystallises in yellow plates or needles, melts at 265—266° with decomposition, and is easily soluble in water, sparingly in alcohol, and insoluble in ether.

Triquinylcarbinol, $OH{\cdot}C(C_9NH_6)_3$, is obtained by oxidation of triquinylmethane with chromic acid in acetic solution. It crystallises in white needles, melts at 108°, dissolves easily in benzene and alcohol, sparingly in light petroleum, and forms easily soluble salts and a yellow, well-crystallised platinochloride. The authors have been unable to obtain dyes from triquinylmethane.

Diquinylketone, $CO(C_9NH_6)_2$, is obtained by heating a mixture of diamidobenzophenone (10 grams), glycerol (29 grams), sulphuric acid (24 grams), and picric acid (3 grams) at 140—150° for four hours. It crystallises from dilute alcohol in long needles, melts at 174°, is easily soluble in alcohol, sparingly in boiling water, forms easily soluble salts, and yields quinoline when heated with soda-lime. The *hydrochloride* forms long, white needles, very soluble in water and alcohol, and melts above 200°; with platinic chloride it yields a sparingly soluble double salt. E. C. R.

Derivatives of Pyrazole. By L. CLAISEN and P. ROOSEN (*Ber.*, **24**, 1888—1894).—3 : 1-Methylphenylpyrazole has been prepared by Knorr (*Annalen*, **238**, 202), and the 5 · 1-derivative by Knorr and

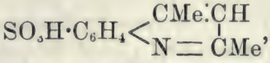
Laubmann (Abstr., 1889. 409). When the methylphenylpyrazole obtained from acetoacetaldehyde (Claisen and Stylos, Abstr., 1888, 671) is cooled by a freezing mixture, it solidifies in part to a crystalline mass which has all the properties of the 3 : 1-derivative (Knorr, *loc. cit.*), and yields on oxidation a phenylpyrazolecarboxylic acid melting at 146°, whilst the phenylpyrazolecarboxylic acid obtained from the liquid portion resembles the 1 : 5-derivative. The methylphenylpyrazole obtained from acetoacetaldehyde is therefore a mixture of the 3 : 1- and 5 : 1-derivatives.

Phenylhydrazine and acetopyruvic acid react together with the formation of a methylphenylpyrazolecarboxylic acid (compare Claisen and Stylos, Abstr., 1888, 676); this crystallises in short prisms containing 1 mol. H_2O, and melts at 106°; the *methyl salt* is a liquid boiling at 255—256° under a pressure of 109 mm.; the amide melts at 146°. The sodium salt has a strongly diuretic action. When heated, the carboxylic acid yields 5 : 1-methylphenylpyrazole, whose identity with that of Knorr and Laubmann (*loc. cit.*) is established by a study of the *methiodide*, the *ethiodide*, and the *platinochloride*, an account of which will be given later.

1 : 5-*Phenylpyrazolecarboxylic acid* is obtained on oxidising the corresponding methylphenylpyrazole with potassium permanganate; it melts at 183°. and is not identical with that obtained by Knorr and Laubmann (*loc. cit.*, 410); the latter must, therefore, have the constitution 1 : 4.

1 : 3 : 5-Phenylpyrazoledicarboxylic acid (Balbiano, Abstr., 1890, 1164) is most conveniently prepared by heating 5 : 1-methylphenylpyrazolecarboxylic acid with a solution of potassium permanganate for 1—2 hours; the acid melts at 266° with decomposition; the *dimethyl salt* melts at 127—128°, and the *diamide* at 190°. When either the dicarboxylic acid or its calcium salt is heated, 1 : 3-phenylpyrazolecarboxylic acid is obtained.

As the 1 : 4-phenylpyrazolecarboxylic acid is the only one which distils with but slight decomposition, it would appear that the carboxyl group is most firmly attached when it occupies the position 4; and it also seems that this group is more firmly attached in the position 3 than in the position 5. It is, therefore, probable that, as in the case of the three pyridinecarboxylic acids, the stability of the phenylpyrazolecarboxylic acids is the greater the further the carboxyl group is removed from the nitrogen atom. Skraup has shown that the melting points of the amidobenzoic acids and of the pyridinecarboxylic acids are the higher the further the carboxyl groups are removed from the nitrogen atom; this applies also to the phenylpyrazolecarboxylic acid, the 1 : 4-acid having the highest melting point.

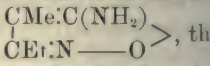
The *dimethylphenylpyrazolesulphonic acid*,  $SO_3H\cdot C_6H_4<\begin{array}{l}CMe{:}CH\\ \qquad\ \ \vert\\ N = CMe\end{array}$, is obtained when acetylacetone is heated with phenylhydrazineparasulphonic acid; it is a crystalline compound, sparingly soluble in water, and yields the corresponding *phenol* on fusion with potash. A description of these and analogous compounds will form the subject of a future communication. A. R. L

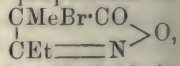
Amidisoxazole. By HANRIOT (*Compt. rend.*, **112**, 796—799).—When propionylpropionitrile is dissolved in concentrated aqueous potash, and the solution is mixed with hydroxylamine hydrochloride, there is considerable development of heat, and an oily liquid separates. This is converted into a crystalline hydrochloride by the action of gaseous hydrogen chloride, and the base is again liberated by the action of potash.

The base has the composition $C_6H_{10}N_2O$; it crystallises in long needles, melts at 44°, and shows great tendency to remain in superfusion, and boils at 180° under a pressure of 200 mm.; it is slightly soluble in water, and insoluble in light petroleum, but dissolves readily in alcohol, ether, or chloroform. The *hydrochloride*, $C_6H_{10}N_2O,HCl$, is crystalline, and the *platinochloride* forms orange octahedra, but both compounds are unstable in solution. When heated with hydrochloric acid at 120°, the base is completely converted into ammonium chloride, hydroxylamine hydrochloride, and diethyl ketone. With acetic chloride, it yields a derivative $C_6H_9AcN_2O$ which melts at 160—162°, and is only slightly soluble in water, ether, or chloroform, but dissolves readily in alcohol or acetone.

Nitrous acid interacts energetically with a solution of the base in dilute hydrochloric acid, and the product separates in yellow lamellæ which melt at 65°, and detonate violently if heated above 100°; it dissolves in alkalis forming a red solution, and is reprecipitated by acids.

A solution of the base in anhydrous ether combines directly with 1 mol. of bromine, and a dibromide separates.

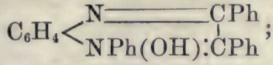
From its mode of formation, the compound should be the oxime of propionylpropionitrile, but the latter would be acid and not basic, and, being saturated, would not combine directly with bromine. Its composition and properties agree with the view that it is an isomeride of the oxime, methylethylamidoisoxazole,  $\left.\begin{array}{l}\mathrm{CMe{:}C(NH_2)}\\ \mid\\ \mathrm{CEt{:}N\text{———}O}\end{array}\right>$, the oxime being first formed, but combining with a molecule of water and undergoing molecular transformation, the molecule of water being afterwards eliminated under the influence of heat or potassium hydroxide.

The product of the action of bromine on the base is amorphous, and is decomposed by water into equal molecular proportions of ammonium bromide and bromomethylethyloxazolone,  $\left.\begin{array}{l}\mathrm{CMeBr{\cdot}CO}\\ \mid\\ \mathrm{CEt{=\!=}N}\end{array}\right>O$, which crystallises in bulky, highly refractive octahedra, insoluble in water, but soluble in alcohol, ether, or chloroform. It melts at 41°, and cannot be distilled even in a vacuum. It dissolves in solutions of alkali hydrogen sulphites, and yields a crystalline compound with hydroxylamine hydrochloride. Sodium amalgam removes all the bromine and yields two crystalline products. C. H. B.

Azonium Bases. By O. N. WITT (*Ber.*, **24**, 1511).—The method for the synthesis of azonium bases recently published by Kehrmann and Messinger (this vol., p. 945) has been described four years ago by the author (Abstr., 1887, 729).

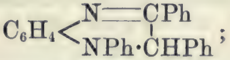
Azonium Bases. By F. KEHRMANN and J. MESSINGER (*Ber.*, **24**, 1799).—A reply to the communication of O. N. Witt (preceding abstract), in which the latter claims priority for the reaction for preparing azonium bases described a short time ago by the authors (this vol., p. 945). They express their regret at their oversight of Witt's previous paper. H. G. C.

Azonium Bases. By F. KEHRMANN and J. MESSINGER (*Ber.*, **24**, 1874—1876; compare preceding abstracts).—The compound obtained by the interaction of benzile and phenylorthophenylenediamine is quite different from that obtained from benzoïn and phenylorthophenylenediamine; the latter compound, prepared according to the method of O. Fischer, melts at 116—117° with previous softening, is insoluble in water and dilute mineral acids, but dissolves in alcohol with a bluish-green fluorescence. The salts are blood-red, and readily undergo dissociation on the addition of water. The relations between the azonium bases, the quinoxaline bases, and the indulones are shown by the following formulæ:—



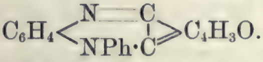
$$C_6H_4{<}\begin{matrix}N{=\!=\!=}CPh\\ NPh(OH){:}CPh\end{matrix};$$

Azonium base from benzile and phenylphenylenediamine.



$$C_6H_4{<}\begin{matrix}N{=\!=}CPh\\ NPh{\cdot}CHPh\end{matrix};$$

Quinoxaline base from benzoïn and phenylphenylenediamine.



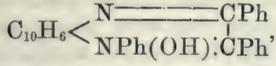
$$C_6H_4{<}\begin{matrix}N{=\!=}C\\ NPh{\cdot}C\end{matrix}{>}C_4H_3O.$$

Indulone from oxyquinone and phenylphenylenediamine.

J. B. T.

A New Class of Fluorescent Colouring Matters of the Quinoxaline Series. By O. FISCHER and M. BUSCH (*Ber.*, **24**, 1870—1874; compare this vol., p. 747).—Reference is made to a recent paper by O. N. Witt (*Ber.*, **24**, 1511), regarding the identity of these quinoxaline derivatives with the azonium bases; since the latter compounds contain oxygen, whilst the former do not, Witt's claim appears to be a mistake.

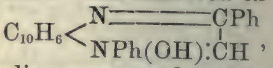
1-2-3-Triphenyl-1-2-hydronaphthaquinoxaline, prepared from benzoïn and β-phenylorthonaphthylenediamine, when treated with ferric chloride, is converted into the corresponding *azonium base*

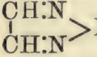
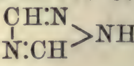
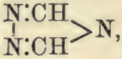
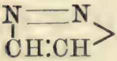


$$C_{10}H_6{<}\begin{matrix}N{=\!=\!=}CPh\\ NPh(OH){:}CPh\end{matrix},$$

which crystallises from alcohol in yellow, lustrous prisms, and melts at 167° with previous softening at 162°. The solution in alcohol, benzene, or ether exhibits a yellowish-green fluorescence; the addition of hydrochloric acid to an alcoholic solution of the base produces a yellow colour. The normal salts are strongly fluorescent in aqueous solution, but this disappears on adding mineral acids. The *nitrate* is sparingly soluble in water, and is deposited in yellow crystals; the *hydrochloride* crystallises from dilute alcohol in dark-yellow needles.

The same base is also formed by heating benzoïn and β-phenylorthonaphthylenediamine with zinc chloride at 200°; the zinc chloride acts, therefore, like acids and facilitates the oxidation of intermediate hydro-derivatives.

1-3-*Diphenylethonaphthazonium bromide* is prepared by heating bromacetophenone with β-phenylorthonaphthylenediamine in alcoholic solution for a short time; it crystallises in lustrous, yellow plates, and exhibits a yellowish-green fluorescence when dissolved in dilute alcohol. The corresponding *hydroxide*,  $\mathrm{C_{10}H_6}<\begin{array}{l}\mathrm{N{=\!=\!=}CPh}\\ \mathrm{NPh(OH){:}CH}\end{array}$, is obtained by the action of soda on the preceding compound, and is deposited from alcohol in lustrous, transparent crystals melting at 148° with previous softening at 100°. In glacial acetic acid or alcoholic solutions, the base is highly fluorescent, but does not show this property when dissolved in ether, benzene, or light petroleum. The *nitrate* crystallises in yellow, silky, lustrous needles, and is sparingly soluble in cold water. J. B. T.

Formation, Properties, and Constitution of Osotriazoles. By H. v. PECHMANN (*Annalen*, **262**, 265—277). — Osotriazole,  $\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{CH{:}N}\end{array}>\mathrm{NH}$, is one of the four isomeric compounds which can, theoretically, be derived from pyrroline by substituting two CH-groups by two atoms of nitrogen; derivatives of two of the three remaining isomerides, namely, of triazole,  $\begin{array}{l}\mathrm{CH{:}N}\\ \mathrm{N{:}CH}\end{array}>\mathrm{NH}$, and of pyrrodiazole,  $\begin{array}{l}\mathrm{N{:}CH}\\ \mathrm{N{:}CH}\end{array}>\mathrm{N}$, are known, but the fourth isomeride,  $\begin{array}{l}\mathrm{N{=\!=}N}\\ \mathrm{CH{:}CH}\end{array}>\mathrm{NH}$, and its derivatives have not yet been prepared.

Three derivatives of osotriazole have been previously described (Abstr., 1888, 1287) as "osotriazone" derivatives; the more suitable term osotriazole will be used in future.

Osotriazole derivatives containing a hydrocarbon radicle in the place of the hydrogen of the imido-group are formed, or can be obtained, by the following reactions:—(1.) By boiling osotetrazones with acids (*loc. cit.*); the yield is about 20 per cent. of the theoretical. (2.) By the decomposition of the phenylosazones, either by boiling with acids or by dry distillation; the yield is small in both cases. (3.) By treating hydrazoximes with phosphorus pentachloride (yield about 20 per cent. of the theoretical), acetic anhydride (yield 25 per cent. of the theoretical), or very dilute alkalis (yield about 50 per cent. of the theoretical). (4.) By the elimination of alcohol from hydrazoximes which are derived from a secondary hydrazine containing at least one fatty radicle; the yield in the only case yet investigated is at least 80 per cent. of the theoretical.

The reactions (3) and (4) are fully described in the following abstracts.

The osotriazole derivatives are yellowish or colourless oils, having a slight alkaloïd-like smell; they boil at a temperature above 200°

without decomposition, and solidify at a low temperature. Osotriazole itself is a feeble acid, but its *n*-alkyl derivatives are weak bases. *n*-Phenylosotriazole and its alkyl substitution products have, generally speaking, the properties of aromatic compounds, and form nitro-, amido-, and sulphonic acid derivatives; on oxidation, the fatty alcohol radicle is converted into the carboxyl-group, which can be eliminated by the usual methods.

The reaction with diazobenzene salts previously described (*loc. cit.*) is not given by pure osotriazoles.

The constitution of the osotriazoles is proved by their methods of formation and by their properties. F. S. K.

Methyl-*n*-phenylosotriazole and its Derivatives. By A. JONAS and H. v. PECHMANN (*Annalen*, **262**, 277—302).—The *acetyl* derivative $\mathrm{NHPh{:}CMe{\cdot}CH{:}N{\cdot}OAc}$ is best prepared by adding dry, finely-divided methylglyoxalphenylhydrazoxime (Abstr., 1889, 47) to acetic anhydride (3 parts) heated at 50°, stirring vigorously until the acetate begins to separate out with development of much heat, and then immediately cooling in a freezing mixture with constant stirring, so that the temperature does not rise above 70—80°. After about 10 minutes, the whole solidifies; the product is then mixed with water, kept until the acetic anhydride is decomposed, and finally washed with water. It crystallises from dilute alcohol in long, flat, colourless needles, melts at 163°, and is readily soluble in acetone, chloroform, boiling alcohol, glacial acetic acid, and benzene, but more sparingly in light petroleum, ether, and carbon bisulphide, and insoluble in water and cold dilute soda; when heated alone or with acetic anhydride, it is converted into methylphenylosotriazole.

Methyl-*n*-phenylosotriazole, previously described as an osotriazone derivative (Abstr., 1888, 1287), is best prepared by boiling the crude acetyl derivative of methylglyoxalphenylhydrazoxime (100 grams, 2 parts) with crystalline sodium carbonate (1 part) and water (30 parts) for 24 hours; after adding a little soda, the oily osotriazole is distilled with steam to free it from resinous substances, methylglyoxalphenylhydrazoxime (10 grams), and the hydrazone of pyruvic acid (10 grams), and the distillate treated with small quantities of an alkaline solution of potassium permanganate until a permanent coloration is produced. The peroxide of manganese is then dissolved by the addition of sodium sulphite and sulphuric acid, the ostriazole distilled with steam, extracted with ether, and purified by fractional distillation; the yield is about 50 per cent. of the acetyl derivative employed. It boils at 149—150° under a pressure of 60 mm., at 242° under the ordinary atmospheric pressure, and its sp. gr. is 1·1071, 17°/4°.

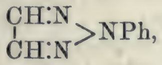
*Trinitromethyl-*n*-phenylosotriazole*, $C_9H_6N_3(NO_2)_3$, is obtained when the preceding compound is introduced into well-cooled, fuming nitric acid (5 parts), concentrated sulphuric acid (5 parts) gradually added, and the mixture then kept at 70—80° until a small portion immediately solidifies when treated with water. It crystallises from alcohol in long, colourless needles, melts at 138°, and is readily soluble in ether, glacial acetic acid, acetone, chloroform, carbon bisulphide, and hot alcohol, but only very sparingly in boiling water, and insoluble in cold water and light petroleum.

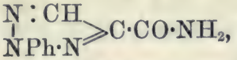
Methyl-n-*phenylosotriazolesulphonic acid* is formed, with development of heat, when the osotriazole is dissolved in fuming sulphuric acid; the barium salt is only moderately easily soluble in cold water, and the sodium salt crystallises from cold water in colourless, hexagonal plates.

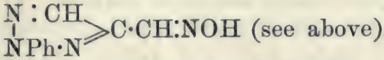
n-Phenylosotriazolecarboxylic acid (20 grams) is produced, together with the corresponding amide (50 grams), small quantities of the nitrile, and phenylosotriazaldoxime (10 grams), when the acetyl derivative, $NOH:CH\cdot C(N_2HPh)\cdot CH:N\cdot OAc$ (100 grams), prepared from dinitrosoacetonehydrazone exactly as described in the case of the glyoxalhydrazoxime, is boiled with 10 per cent. sodium carbonate (1 litre) for 24 hours; on cooling, the oily mixture of the neutral products solidifies to a mass of crystals, and is separated from the alkaline solution of the acid by filtration. The filtrate is treated first with potassium permanganate, and then with sodium sulphite and sulphuric acid as described above, and the precipitated acid separated by filtration. The crystalline mixture of the neutral products is agitated with soda to dissolve the aldoxime, and the insoluble residue then dissolved in boiling benzene, from which, on cooling, the amide is deposited almost completely, whilst the nitrile remains in solution. When the acid is the desired prdouct, this separation is unnecessary; the mixture of acid and neutral products is boiled with soda until the evolution of ammonia is at an end and the amide and nitrile are completely converted into the acid, and the cold solution is saturated with carbonic anhydride to precipitate the aldoxime. The filtrate is then treated with potassium permanganate, and the acid isolated as before; the yield of acid is 65 grams, and of aldoxime 8 grams. In the above reaction, the first product is phenylosotriazaldoxime; this compound is converted into the nitrile by the elimination of water, then into the amide, and finally into the acid.

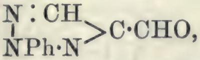
n-*Phenylosotriazolecarboxylic acid* prepared in this way melts at 191—192°, and is identical with the acid obtained by oxidising methylphenylosotriazole (*loc. cit.*). The *potassium* salt, $C_9H_6N_3O_2K + H_2O$, crystallises from 90 per cent. alcohol in efflorescent plates. The *barium* salt, $(C_9H_6N_3O_2)_2Ba + 2H_2O$, crystallises from hot water in transparent plates; the *cadmium* salt, $(C_9H_6N_3O_2)_2Cd + 2H_2O$, in long, colourless needles. The *methyl* salt, $C_{10}H_9N_3O_2$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, crystallises from methyl alcohol in long, colourless needles, melts at 89—90°, boils at 285—286°, and is soluble in most ordinary solvents. The *ethyl* salt, $C_{11}H_{11}N_3O_2$, crystallises in lustrous needles, melts at 59°, and boils at 305—307°.

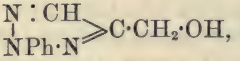
When phenylosotriazole or its homologues is treated with sodium in boiling alcoholic solution, it seems to be converted into hydroderivatives; traces of ammonia and aniline are formed, but no fatty diamine. Phenylosotriazolesulphonic acid is decomposed by sodium amalgam in boiling alcoholic solution, yielding ammonia and sulphanilic acid, but fatty diamines are not formed. When phenylosotriazolecarboxylic acid (10 grams) is treated with 4 per cent. sodium amalgam (280 grams) in alkaline solution, it is decomposed into hydrogen cyanide and phenylhydrazidoacetic acid (5 grams); the last-named compound melts at 159°, and is identical with the acid obtained by Elbers (*Annalen*, **227**, 353) by the reduction of the hydrazone of glyoxylic acid.

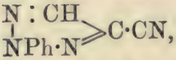
n-*Phenylosotriazole*,  $\begin{array}{l}\mathrm{CH{:}N}\\ \mid\\ \mathrm{CH{:}N}\end{array}\!>\!\mathrm{NPh}$, is obtained, together with aniline and hydrogen cyanide, when the silver salt of phenylosotriazolecarboxylic acid is submitted to dry distillation; the yield is 3 grams from 15 grams of the silver salt. It can also be prepared by warming glyoxalosotetrazone (Abstr., 1888, 1287) with ferric chloride and hydrochloric acid until it is completely converted into a brown oil; the yield is 3·5 grams from 20 grams of the crude tetrazone. It is an almost colourless oil, boils at 223—224° (716 mm.), and is volatile with steam; it is readily soluble in ordinary organic solvents and in concentrated mineral acids, but only sparingly in water, dilute acids, and alkalis. It is not acted on by potassium permanganate. When boiled with sodium in alcoholic solution, it gives a solution which gradually turns red on cooling. The *nitro*-compound, $C_8H_6N_3{\cdot}NO_2$, is formed when the osotriazole is treated with well-cooled, fuming nitric acid, and the mixture then warmed for a few minutes on the water-bath; it crystallises from alcohol in colourless needles, melts at 183—184°, and is readily soluble in ether, acetone, chloroform, and benzene.

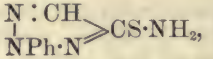
n-*Phenylosotriazolecarboxylamide*,  $\begin{array}{l}\mathrm{N:CH}\\ \mid\\ \mathrm{NPh{\cdot}N}\end{array}\!\geqslant\!\mathrm{C{\cdot}CO{\cdot}NH_2}$, prepared as described above, crystallises from water in lustrous needles, melts at 143·5°, and is readily soluble in alcohol, ether, acetone, chloroform, glacial acetic acid, and hot benzene, but only sparingly in light petroleum; on distillation with zinc-dust, it is converted into the corresponding nitrile.

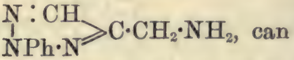
n-Phenylosotriazaldoxime,  $\begin{array}{l}\mathrm{N:CH}\\ \mid\\ \mathrm{NPh{\cdot}N}\end{array}\!\geqslant\!\mathrm{C{\cdot}CH{:}NOH}$ (see above), melts at 115° (compare Pechmann and Wehsarg, Abstr., 1889, 35).

n-*Phenylosotriazaldehyde*,  $\begin{array}{l}\mathrm{N:CH}\\ \mid\\ \mathrm{NPh{\cdot}N}\end{array}\!>\!\mathrm{C{\cdot}CHO}$, is formed when the aldoxime is boiled for a short time with dilute sulphuric acid; the product is distilled with steam and purified by dissolving it in a solution of sodium hydrogen sulphite. It melts at 70°, distils without decomposition, and is soluble in most ordinary solvents except water; it has a pungent odour, gives the usual reactions of aldehydes, and dissolves unchanged in dilute alkalis. The *hydrazone*, $C_{15}H_{13}N_5$, is precipitated on adding phenylhydrazine to a dilute aqueous solution of the aldehyde; it crystallises from alcohol in colourless plates, sinters together at 109—110°, and melts between 118° and 140° according to the manner in which it is heated. It is readily soluble in alcohol, ether, acetone, glacial acetic acid, chloroform, benzene, and carbon bisulphide, but only sparingly in light petroleum, and insoluble in water and dilute soda; it dissolves in concentrated sulphuric acid, yielding a yellowish-red solution, which turns dark blue on the addition of ferric chloride.

n-*Phenylosotriazyl alcohol*,  $\begin{array}{l}N:CH\\ |\\ NPh{\cdot}N\end{array}\!\!>C{\cdot}CH_2{\cdot}OH$, is formed, together with phenylosotriazolecarboxylic acid, when the aldehyde is treated with soda at the ordinary temperature. It crystallises from a mixture of chloroform and light petroleum in small, colourless prisms, melts at 67°, and is very readily soluble in alcohol, ether, glacial acetic acid, acetone, and hot light petroleum, but rather more sparingly in chloroform and benzene, and only very sparingly in cold water; it dissolves unchanged in warm, dilute soda, and with concentrated sulphuric acid it gives a pale-yellow solution.

Cyano-n-*phenylosotriazole*,  $\begin{array}{l}N:CH\\ |\\ NPh{\cdot}N\end{array}\!\!>C{\cdot}CN$, is formed in the preparation of phenylosotriazolecarboxylic acid as described above; it can also be obtained by distilling the corresponding amide with zinc-dust, and by treating glyoxylylcyanosotetrazone (Abstr., 1889, 47) with acids, but it is best prepared by boiling the acetyl derivative of dinitrosoacetonehydrazone with acetic anhydride for about two hours. It crystallises from dilute alcohol in colourless plates, melts at 94·5°, and boils at 190—192° under a pressure of 60 mm.; it has an odour recalling that of benzonitrile, is readily volatile with steam, and dissolves freely in ether, acetone, glacial acetic acid, chloroform, benzene, and carbon bisulphide, but is only sparingly soluble in cold alcohol and light petroleum, and insoluble in water and dilute alkalis.

n-*Phenylosotriazolethiamide*,  $\begin{array}{l}N:CH\\ |\\ NPh{\cdot}N\end{array}\!\!>CS{\cdot}NH_2$, is precipitated in long, yellowish needles when hydrogen sulphide is passed for some time into a hot ammoniacal solution of the nitrile, and the solution then mixed with water; it melts at 131—132°, darkens on exposure to the air, and is readily soluble in ether, alcohol, acetone, chloroform, glacial acetic acid, and carbon bisulphide, but more sparingly in light petroleum, and insoluble in cold water.

n-*Phenylosotriazylamine*,  $\begin{array}{l}N:CH\\ |\\ NPh{\cdot}N\end{array}\!\!>C{\cdot}CH_2{\cdot}NH_2$, can be obtained by reducing the thiamide with zinc and hydrochloric acid in alcoholic solution, and decomposing the product with soda. It is a colourless oil, boils at 222—223° under a pressure of 100 mm., and is readily soluble in alcohol, ether, acetone, and chloroform, but only sparingly in water and light petroleum. It absorbs carbonic anhydride from the air with great avidity, being thereby converted into a crystalline *carbonate* of the composition $(C_9H_{10}N_4)_2,H_2CO_3$. The *hydrochloride*, $C_9H_{10}N_4,HCl$, crystallises from cold water in plates, melts at 228—229°, and is readily soluble in alcohol and water. The *platinochloride*, $(C_9H_{10}N_4)_2,H_2PtCl_6$, crystallises from water in long, yellow prisms, and is readily soluble in hot, but only sparingly in cold, water. The tartrate forms well-defined, transparent crystals. On adding carbon bisulphide to an ethereal solution of the base, a compound melting at 122—123° is precipitated; nitrous acid converts the base into the alcohol described above.

F. S. K.

Homologues of *n*-Phenylosotriazole. By O. BALTZER and H. v. PECHMANN (*Annalen*, **262**, 302—313).—*Diacetylphenylhydrazacetoxime*, $\mathrm{N_2HPh{:}CMe{\cdot}CMe{:}N{\cdot}OAc}$, is prepared from diacetylphenylhydrazoxime, exactly as described in the case of methylglyoxalhydrazoxime (compare preceding abstract); it crystallises from alcohol in yellowish plates and melts at 171°.

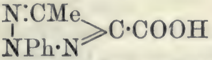
Dimethyl-*n*-phenylosotriazole, previously described as an osotriazone derivative (Abstr., 1888, 1287), is best prepared by boiling the preceding compound with sodium carbonate; the product is separated from regenerated diacetylphenylhydrazoxime and obtained in a pure condition by the same methods as those used in the case of methyl phenylosotriazole (compare preceding abstract); the yield is 30 per cent. of the hydrazoxime employed.

Diacetyldiphenylhydrazoxime, $\mathrm{NPh_2{\cdot}N{:}CMe{\cdot}CMe{:}NOH}$, crystallises in small, colourless prisms and melts at 126—127°; it cannot be converted into an osotriazole derivative under any conditions.

Diacetylmethylphenylhydrazoxime, $\mathrm{NMePh{\cdot}N{:}CMe{\cdot}CMe{:}NOH}$, is precipitated as an oil on adding a solution of methylphenylhydrazine sulphate (34 grams) and sodium acetate (55 grams) in water (310—360 grams) and glacial acetic acid (20 grams) to a solution of methylnitrosoacetone (20 grams) in water (120 grams); the yield is quantitative. It crystallises from dilute alcohol in yellowish needles, melts at 105·5°, and dissolves in alkalis and acids with a yellow coloration; it is decomposed by boiling dilute sulphuric acid with formation of diacetyl, and it gives a cherry-red coloration with nitrous acid; its solution in concentrated sulphuric acid is coloured red on the addition of ferric chloride. The acetyl derivative is a liquid. When diacetylmethylphenylhydrazoxime is boiled with acetic anhydride, it is decomposed into dimethyl-*n*-phenylosotriazole and methyl alcohol; the yield of the former is more than 80 per cent. of the theoretical.

*Dinitrodimethyl-*n*-phenylosotriazole*, $\mathrm{C_{10}H_9N_3(NO_2)_2}$, is formed when a solution of the osotriazole in concentrated nitric acid (6 parts) is mixed with concentrated sulphuric acid (9 parts); it crystallises from alcohol in yellow needles and melts at 139°. A mixture of warm, fuming nitric acid and concentrated sulphuric acid converts the osotriazole into a compound, probably a trinitro-derivative, which melts at 227°.

*Methyl-*n*-phenylosotriazolecarboxylic acid*,



$\mathrm{\begin{array}{l}N{:}CMe\\ \;|\\ NPh{\cdot}N\end{array}\!\!>C{\cdot}COOH}$

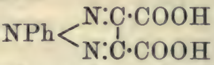
(5 grams), is formed, together with *n*-phenylosotriazoledicarboxylic acid (2 grams), when dimethylphenylosotriazole (10 grams) is boiled with an alkaline solution of potassium permanganate (40 grams) for 12 hours; the two compounds are separated by taking advantage of the fact that the sodium salt of the monocarboxylic acid is soluble, that of the dicarboxylic acid insoluble, in alcohol. It crystallises from dilute alcohol in long needles, melts at 198°, and is readily soluble in

alcohol, but only sparingly in water. The *silver* salt, $C_{10}H_8N_3O_2Ag$, is a colourless compound, sparingly soluble in hot water. The *calcium* salt and the *barium* salt crystallise from hot water in small needles; the *zinc*, *manganese*, and *cadmium* salts are only sparingly soluble in boiling water.

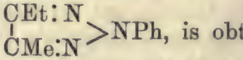
Ethyl methylphenylhydrazonitrosoacetoacetate,

$$\mathrm{NMePh\cdot N{:}CMe\cdot C(NOH)\cdot COOEt},$$

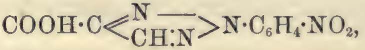
prepared by treating ethyl nitrosoacetoacetate with methylphenylhydrazine, separates from a mixture of chloroform and light petroleum in the form of a light-yellow, crystalline powder, and melts at 77—80°; when it is boiled with acetic anhydride, and the product hydrolysed with soda, methylphenylosotriazolecarboxylic acid is obtained; the yield is almost quantitative.

Phenylosotriazoledicarboxylic acid,  $\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{N{:}C\cdot COOH}\\ \quad\;\vert\\ \mathrm{N{:}C\cdot COOH}\end{array}$ (see above), separates from boiling water in the form of a colourless, crystalline powder, and melts at 255—256° with liberation of water and formation of the anhydride (m. p. 104°); it gives the fluoresceïn reaction with resorcinol. The *silver* salt, $C_{10}H_5N_3O_4Ag_2$, crystallises from boiling water in thread-like forms. The *calcium* salt and the *cadmium* salt are only sparingly soluble, but the *zinc* salt and the *manganese* salt are readily soluble, in water.

Acetylpropionyl-αβ-phenylhydrazacetoxime, $\mathrm{N_2HPh{:}CMe\cdot CEt{:}N\cdot OAc}$, prepared from ethyl ethylacetoacetate, crystallises from alcohol in long, colourless needles and melts at 147—148°.

Methylethyl-n-*phenylosotriazole*,  $\begin{array}{l}\mathrm{CEt{:}N}\\ \vert\\ \mathrm{CMe{:}N}\end{array}\!\!>\mathrm{NPh}$, is obtained by boiling the preceding compound with water; it melts below 0° and boils at 270°. The *dinitro*-derivative, $C_{11}H_{11}N_3(NO_2)_2$, crystallises from alcohol in lustrous needles and melts at 113°. When methylethylphenylosotriazole is treated with an alkaline solution of potassium permanganate, it is rapidly oxidised, yielding methylphenylosotriazolecarboxylic acid (m. p. 198°) and small quantities of a dicarboxylic acid. F. S. K.

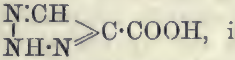
Osotriazole. By O. BALTZER and H. v. PECHMANN (*Annalen*, **262**, 314—323).—*Nitro*-n-*phenylosotriazolecarboxylic acid*,

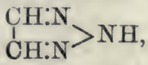


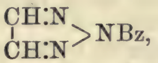
$$\mathrm{COOH\cdot C}\Big\langle\begin{array}{l}\mathrm{N\;\text{——}}\\ \mathrm{CH{:}N}\end{array}\Big\rangle\mathrm{N\cdot C_6H_4\cdot NO_2},$$

is obtained when phenylosotriazolecarboxylic acid (compare Jonas and Pechmann, this vol., p. 1111) is dissolved in fuming nitric acid (10 parts), the solution kept for half an hour and then poured on to ice; it crystallises from glacial acetic acid in yellowish needles, melts at 236°, and is soluble in hot alcohol, but more sparingly in ether, chloroform, and boiling water. The *ammonium* salt crystallises in long needles, and is comparatively sparingly soluble, but the *sodium* salt and the *potassium* salt are readily soluble, in water; the salts of the heavy metals are insoluble.

Amido-n-*phenylosotriazolecarboxylic acid*, $C_9H_6N_3O_2{\cdot}NH_2$, is prepared by reducing the nitro-compound with stannous chloride and hydrochloric acid; it separates from glacial acetic acid in the form of a colourless, crystalline powder, and from dilute alcohol in needles, melts at 252° with decomposition, and is readily soluble in hot water, the solution darkening on boiling. In aqueous solutions of the acid, a solution of bleaching powder produces first a reddish-brown coloration and then a yellow, flocculent precipitate. The *ammonium* salt crystallises from alcohol in long, flat needles; the *calcium*, *barium*, and *manganese* salts crystallise well, but the salts of most of the heavy metals are insoluble.

Osotriazolecarboxylic acid,  $\genfrac{}{}{0pt}{}{\text{N:CH}}{\text{NH}{\cdot}\text{N}}\!\geqslant\!\text{C}{\cdot}\text{COOH}$, is formed, together with a considerable quantity of another acid, probably an azoxy-derivative, when a warm saturated solution of potassium permanganate is added to a warm, dilute alkaline solution of the amido-acid until a permanent coloration is produced; after decolorising with alcohol, the filtered solution is concentrated by evaporation, acidified with acetic acid, and the oxalic acid precipitated with calcium chloride; the filtrate is then treated with a solution of copper acetate in slight excess, the precipitated copper salt washed well with cold water, decomposed with hydrogen sulphide, and the filtered solution evaporated, when the osotriazolecarboxylic acid is deposited in grey crystals. It separates from water in the form of a colourless, crystalline powder, melts at 211°, decomposes at a higher temperature with evolution of carbonic anhydride, and is readily soluble in boiling water, but only sparingly in alcohol and cold water, and practically insoluble in ether, chloroform, glacial acetic acid, and acetone. It is only very slowly oxidised by potassium permanganate, is not acted on by nitrous acid, or by boiling fuming nitric acid, and crystallises unchanged from hot hydrochloric acid. The *calcium* salt, $(C_3H_2N_3O_2)_2Ca + 2H_2O$, crystallises from hot water in prisms; the salts of the alkalis are readily soluble and the silver salt is explosive.

Osotriazole,  $\genfrac{}{}{0pt}{}{\text{CH:N}}{\text{CH:N}}\!>\!\text{NH}$, can be prepared by distilling the dry carboxylic acid, in small quantities at a time, from a retort heated at 230—240° in a metal-bath; if the retort is heated over the free flame, explosions are liable to occur; the yield is almost quantitative. It is a colourless oil, having a slight, alkaloïd-like smell, and a sweetish, repulsive taste; it melts at 22·5°, boils at 203—204° (715 mm.), and is soluble in water and most ordinary solvents, except light petroleum, in all proportions; the aqueous solution has a neutral reaction. The *hydrochloride*, $C_2H_3N_3,HCl$, is a colourless, crystalline powder, and is decomposed by water; the *platinochloride* is very unstable. The *silver* derivative, $C_2H_2N_3Ag$, is precipitated on adding silver nitrate to an aqueous solution of osotriazole; it is insoluble in ammonia, but soluble in nitric acid, and it explodes when heated. The compound $C_2H_2N_3HgCl$, prepared by precipitating a solution of osotriazole with mercuric chloride, crystallises in lustrous needles, is soluble in hydrochloric acid, and burns when heated on platinum foil, leaving a very voluminous ash. In an aqueous solution of osotriazole, copper sulphate produces a blue precipitate which dissolves in excess of the reagent, yielding a blue solution; a calcium derivative, which is decomposed by carbonic anhydride, is formed when calcium hydroxide is added to an aqueous solution of osotriazole. Sodium dissolves in an ethereal solution of osotriazole, yielding a solid sodium derivative.

Benzoylosotriazole,  $\begin{matrix}\text{CH:N}\\ | \\ \text{CH:N}\end{matrix}\!>\!\text{NBz}$, is precipitated in the form of a colourless, crystalline powder, when an aqueous solution of osotriazole is shaken with 10 per cent. soda and benzoic chloride; it separates from chloroform and ether in lustrous crystals, melts at 100°, and is decomposed by soda and by boiling alcohol. The corresponding acetyl derivative is a colourless liquid. F. S. K.

Alkylation of Secondary and Primary Bases by Potassium Alkyl Sulphates. By M. PASSON (*Ber.*, **24**, 1678—1682).—*Methyl coniine* is obtained by adding a concentrated solution of potassium methyl sulphate (25 grams) to a concentrated solution of coniine (9 grams) and heating on the water-bath until the mixture reacts neutral. The unaltered coniine is separated by conversion into its nitroso-compound and extraction with ether; the solution is made alkaline and distilled, the base precipitated from the distillate with sodium hydroxide, dried over potash, and distilled. The pure base is a colourless oil, which floats on water, boils at 175·5°, and smells like coniine. The *hydrochloride* is similar to coniine hydrochloride, but melts at 188—189°. When heated at 240°, it sublimes in white needles, is easily soluble in water and alcohol, crystallises from the latter in beautiful, white needles, and has the same physiological action as coniine hydrochloride. The *aurochloride* is insoluble in cold, sparingly soluble in hot, water, and separates first as an oil, afterwards in long, slender needles, and melts at 79°. The *platinochloride* is easily soluble, insoluble, however, in a mixture of ether and alcohol, and melts at 158—160°.

Dipropylmethylamine is obtained from normal dipropylamine in a similar way to the above base. It boils at 117°. The *platinochloride* crystallises from water in beautiful, orange-red needles and melts about 200°.

Dipropylethylamine is obtained in a similar way to the methyl compound. The reaction, however, does not take place so easily, and a large excess of potassium ethyl sulphate must be used. It boils at 132—134° and is sparingly soluble in water. The *platinochloride* is easily soluble in water, but insoluble in a mixture of ether and alcohol. The *aurochloride* is fairly easily soluble in water, crystallises in beautiful needles, and melts at 96°.

Diethylmethylamine, obtained in a similar way, is a colourless liquid, smells like trimethylamine, and boils at 63—65°. The *hydrochloride* forms large, colourless plates, and is extremely soluble. The *aurochloride* crystallises in short, yellow needles and is fairly soluble in water. The methyldiethylamine, prepared from methylamine and potassium ethyl sulphate, boils at 63—66° and gives a similar aurochloride. E. C. R.

New Alkaloïd from Conium maculatum. By A. Ladenburg and G. Adam (*Ber.*, **24**, 1671—1676).—The authors have received from E. Merck a new alkaloïd obtained from *Conium maculatum*. The preparation was a white powder, easily soluble in water, alcohol, ether, and benzene, and yielded salts with acids. It was purified by distillation and by crystallisation from toluene; both methods gave identical products. Analysis gave numbers agreeing with the formula $C_8H_{17}NO$. Since the new base is very like conhydrine, and probably has a similar constitution, the authors have called it pseudoconhydrine.

Pseudoconhydrine is a strong base, reacts alkaline, yields easily soluble salts, boils at 229—231° (uncorr.), melts at 100—102°, and sublimes in slender needles. It is, like conhydrine, a secondary base, since the hydrochloride, when warmed with sodium nitrite, yields a nitrosamine. The *hydrochloride* forms colourless, hygroscopic crystals, easily soluble in water and alcohol, and also soluble in ether. The *hydrobromide* crystallises in tablets.

When pseudoconhydrine is heated with fuming hydriodic acid and amorphous phosphorus for eight hours at 180°, an *iodide* of the formula $C_8H_{16}NI,HI$ is obtained. It crystallises from water in nodular aggregates, darkens at 143°, melts at 155°, and yields on reduction a volatile base, but, owing to the small amount of material, this was not examined. When heated with fuming hydrochloric acid, it also yields a base easily volatile with steam.

From the above results, the authors conclude that pseudoconhydrine belongs to the class of alkines, and has a constitution analogous to that of conhydrine. The authors attempted to synthesise the compound by reduction of the condensation product of α-ethylpyridine with formaldehyde with the following results:—

α-Lutidylalkine, $C_5NH_4{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained by heating α-ethylpyridine with formaldehyde and water for eight hours at 160°. The product is freed from unaltered ethylpyridine by steam distillation, extracted with chloroform, the solution dried with potassium carbonate, the chloroform distilled off, and the residue distilled under reduced pressure. It boils at 128—131° under 17 mm. pressure, and is easily soluble in water and alcohol, sparingly in ether. The *platinochloride*, $(C_8H_{11}NO)_2,H_2PtCl_6$, is easily soluble and melts at 142°. The *aurochloride* is sparingly soluble, crystallises from water in ill-characterised, yellow crystals, and melts at 71°.

α-Lupetidylalkine, $C_5NH_{10}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is obtained by reduction of the above base in absolute alcohol with sodium. It is purified by extraction with ether and distillation, boils at 232—234° under the ordinary pressure, and closely resembles pseudoconhydrine in boiling point, odour, and solubility, but has a much lower melting point, and does not yield crystalline salts. Lupetidylalkine will not crystallise either when sown with crystals of conhydrine or pseudoconhydrine; when cooled with solid carbonic anhydride and ether, it crystallises, but melts again below 0°. Neither the hydrochloride

nor hydriodide is crystalline. The hydrobromide crystallises, after remaining some time in the desiccator, in feathery crystals which liquefy on exposure to air. When reduced with fuming hydriodic acid and amorphous phosphorus, a base is obtained which is volatile with steam, and yields a sparingly soluble aurochloride crystallising in silky needles and melting at 118—119°. Analysis gave numbers corresponding to the formula $C_8H_{15}N,HAuCl_4$.

Hence lupetidylalkine is not identical either with conhydrine or with pseudoconhydrine. E. C. R.

Paraxanthine. By G. Salomon (*Zeit. physiol. Chem.*, **15**, 319—320). —Paraxanthine crystals have been previously described by the author (*Zeit. klin. Med.*, **7**, 72) as containing no water of crystallisation. In another preparation of these crystals, it is now proved that some of them on being heated to 110° become cloudy and whitish from loss of water, while others, isomorphous with them, remain bright. Owing to the admixture, it was not found possible to determine the water of crystallisation quantitatively. W. D. H.

Violet Colouring Matter Derived from Morphine. By P. Cazeneuve (*Compt. rend.*, **112**, 805—807).—Seven grams of morphine are boiled for 100 hours in a reflux apparatus with an equal molecular proportion (5 grams) of paranitrosodimethylaniline hydrochloride and 500 c.c. of methyl alcohol. A crystalline compound separates, having all the properties of the tetramethyldiazoamidobenzene formed by the action of aniline on paranitrosodimethylaniline. The alcoholic liquid is evaporated to dryness, the residue treated with hot water, the solution filtered, the filtrate again evaporated to dryness, and dissolved in dilute hydrochloric acid. A violet solution is thus obtained, from which sodium hydroxide precipitates the base; the latter, after being washed free from morphine, is treated with amyl alcohol, which dissolves the violet compound, but leaves a blue substance undissolved. Analysis of the platinochloride, precipitated by a mixture of alcohol and ether, shows that the violet compound has the composition $C_{17}H_{19}NO_4{\dot{:}}N{\cdot}C_6H_4{\cdot}NMe_2$. The free base is amorphous, and is slightly soluble in water, from which it is precipitated by addition of sodium chloride; it is readily soluble in methyl, ethyl, or amyl alcohol, yielding strongly dichroic solutions which are violet by transmitted, and red by reflected, light. It dyes wool, silk, and guncotton directly, giving a beautiful bright violet, which, however, fades when exposed to light.

This colouring matter is not a safranine, but seems comparable to dimethylamidodiphenylimide (Bindschedler's green). Substitution does not take place in the phenol group, for a similar product is obtained from codeïne, the methyl group in which would prevent condensation by union of the oxygen with nitrogen. It is probable that the formation of the violet compound is due to the tendency of the morphine to form oxymorphine. At the same time, its formation and character invalidate Polstorff's view that pseudomorphine is formed from 2 mols. of morphine with elimination of 2 atoms of hydrogen; if this were so, the pseudo-compound should yield a safranine, and not an indamine. It is also possible to regard the colouring matter as a phenanthrene derivative. C. H. B.

Pseudocodeïne. By E. MERCK (*Arch. Pharm.*, **229**, 161—164). —*Pseudocodeïne*, $C_{18}H_{21}NO_3 + H_2O$, a strong base discovered during the preparation of apocodeïne, forms a white, crystalline mass, easily soluble in alcohol, especially when hot. From this solution it is precipitated by water in white needles. It is sparingly soluble in ether, from which solution it separates in brilliant, transparent needles. It melts at 178—180° (uncorr.). A 1·91 per cent. alcoholic solution rotates the plane of polarisation 1·423° towards the left; hence its specific rotatory power is −91·040°. Ferric chloride gives no reaction. The base yields well-crystallisable salts, of which the hydrochloride, hydrobromide, nitrate, platinochloride, mercurochloride, and picrate are described. The physiological action of pseudocodeïne is similar to that of codeïne, but weaker. J. T.

Conversion of Cupreïne into Quinine. By E. GRIMAUX and A. ARNAUD (*Compt. rend.*, **112**, 774—775).—When cupreïne, perfectly free from quinine, is boiled for several hours in a reflux apparatus, with an equivalent quantity of sodium and an excess of methyl iodide dissolved in methyl alcohol, quinine methiodide is obtained in slender, white needles, and quinine dimethiodide in yellow prisms, identical in composition, melting point, and rotatory power with the methiodides obtained from natural quinine. The methiodides from both sources dissolve in dilute sulphuric acid with a beautiful blue fluorescence.

If the cupreïne is heated in sealed tubes at 100° for about 12 hours with sodium methoxide and methyl chloride, free quinine is obtained identical in all its properties with the natural product.

It follows that cupreïne is a substance with a phenolic function, and quinine is its methyl ether. This result throws little light upon the constitution of quinine, but establishes the presence of a methoxy-group OMe. It is remarkable that a methyl group is frequently found in the products obtained from plants, whilst an ethyl group never occurs. This is, doubtless, due to the mode of nutrition of plants, which absorb carbonic anhydride, and convert it first into formaldehyde and afterwards into methyl alcohol. C. H. B.

Isocinchonine. By E. JUNGFLEISCH and E. LÉGER (*Compt. rend.*, **112**, 942—945).—Chiefly polemical and a question of priority. The isocinchonine obtained by Hesse's method (Abstr., 1888, 379) is a mixture of cinchonigine, cinchoniline, and a non-crystallisable base.

C. H. B.

Tropine. By A. LADENBURG (*Ber.*, **24**, 1628—1633).—The first part of this paper contains crystallographic descriptions and measurements of tropine platinochloride and *tropine aurochloride*. The former belongs to the monosymmetric system; the latter melts at 202°, and is deposited in pale-yellow, transparent crystals of the asymmetric system. *Tropine mercurochloride*, $C_8NH_{15}O,HCl,6HgCl_2$, melts at 246°.

With reference to the production of the bibasic tropic acid by the oxidation of tropine, the author points out that in the case of piperidine, pipecoline, and coniine, the piperidine ring is resolved and an α-carbon atom oxidised to carboxyl; as tropine contains a carboxyl group in the side chain, this would probably undergo change and yield a bibasic acid; hence the formation of tropic acid, contrary to the opinion of Liebermann, is not opposed to the author's formula for tropine (compare this vol., p. 749). J. B. T.

Amarylline and Bellamarine, two new Alkaloïds. By K. Fragner (*Ber.*, **24**, 1498—1500).—It has long been known that the plants of the family *Amaryllideæ* are poisonous, but hitherto they have not been chemically examined. The author finds that the bulbs of *Amaryllis formosissima*, which is indigenous to South America, contain a new alkaloïd, for which he proposes the name *amarylline.* It crystallises from alcohol in aggregates of short needles, is slightly soluble in water, readily in chloroform and ether. It gives precipitates with the usual alkaloïdal reagents, and shows a characteristic reaction with sulphuric acid, giving a reddish-brown solution, which passes after a long time into brown, and becomes green on addition of a little water. The alkaloïd becomes yellow at 190°, brown at 194°, and melts completely at 196°.

Another alkaloïd, which the author terms *bellamarine*, may be obtained from the bulbs of *Amaryllis belladonna*, and crystallises in colourless needles, readily soluble in chloroform, alcohol, and ether. It becomes yellow at 175°, brown at 179°, and melts at 181°. With sulphuric acid, it gives a grey coloration, which becomes a beautiful red on warming, and yellowish-green on addition of a grain of potassium nitrate. With sulphuric acid and a little potassium dichromate, it gives first a yellowish-green and then a brown coloration.

H. G. C.

Morrenine. By P. Arata and C. Gelzer (*Ber.*, **24**, 1849—1851). —The authors have examined the roots of *Morrenia brachystephana* (tásis), the sap of which is employed in the Argentine Republic as a specific for deficient lacteal secretion. The finely divided roots were extracted with ether, which removes wax, fatty acids, and resinous substances; one of the latter is soluble in alcohol and melts at 60°. The exhausted roots are boiled with alcohol, the solution filtered, and the alcohol removed; the residue contains a new alkaloïd which has a very bitter taste, is readily soluble in water, chloroform, or amyl alcohol, and melts at 106°. Precipitates are obtained with all the ordinary alkaloïdal reagents, and it is proposed to term it *morrenine.* The compound may be prepared more readily by digesting the roots for three to four days with 2 per cent. hydrochloric acid, neutralising the filtered solution with magnesia, evaporating to dryness, and extracting the residue with warm alcohol. (See also p. 1088.) J. B. T.

Crystalline Egg Albumin. By S. Gabriel (*Zeit. physiol. Chem.*, **15**, 456—464).—In a repetition of Hofmeister's (Abstr., 1890, 182) work, a half saturated solution of ammonium sulphate was found to be too strong, causing precipitation. The proteïd was dissolved in water, and then a saturated solution of ammonium sulphate added until a cloudiness appeared, which was dissolved on adding a little more water. The formation of all stages of crystallisation can then be easily observed. The "globuliths" which are first formed soon loose their homogeneity and show a radiating appearance. The sphæroliths are bundles of needles which soon separate. After drying, the proteïd is no longer crystalline. Drawing an analogy from Pawlewski's experiments on paraffin dissolved in acetic acid (*Ber.*, **23**, 327), it is believed that colloïdal proteïd is a polymeride of the crystalline material. The question whether these crystals were composed of pure albumin or of albumin in combination with ammonium sulphate was left open by Hofmeister. Harnack (this vol., 476) states they contain only 5 per cent. of proteïd. In the present research their composition was found to be as follows :—

Egg albumin	80·86	in 100 parts.
Ammonium sulphate	15·56	
Water	3·39	
Ash	0·19	

The percentage of nitrogen in pure egg albumin is 14·96. It thus appears to contain less nitrogen than other proteïds. W. D. H.

Artificial Melanin. By G. POUCHET (*Compt. rend.*, **112**, 884—885).—A substance having the general properties of the melanins is found in old anatomical preparations preserved in alcohol, and is also obtained by treating fresh blood with alcohol and mercuric chloride; the exact conditions which determine its formation have not yet been ascertained. It forms black grains insoluble in alcohol, ether, carbon bisulphide, and hydrochloric acid. Since all other constituents of blood are soluble in hydrochloric acid, the melanin can easily be separated from them. The grains dissolve in a 2 per cent. solution of potash, but a flocculent, brownish substance is precipitated on addition of hydrochloric acid; they dissolve in sulphuric acid forming a reddish solution, or if the acid is slightly diluted, a ponceau-coloured solution. Hydrogen peroxide or chlorine-water bleaches the grains, and they are then seen to have a radiating structure. In contact with hydrochloric acid and potassium ferrocyanide, they give no blue coloration. C. H. B.

Physiological Chemistry.

A New Method for Estimating the Specific Gravity of the Blood. By J. B. HAYCRAFT (*Proc. Roy. Soc. Edin.*, **18**, 251—254).—The advantages of the new method are accuracy, small amount of apparatus, speed, and that only one drop of blood is required. Two

mixtures of benzyl chloride (sp. gr. 1·100) and toluene (sp. gr. 0·8706) are made, one (*a*) having a sp. gr. of 1·070, and the other (*b*) having a sp. gr. of 1·020 : 1 c.c. of (*a*) is measured off in a pipette graduated to 0·01 c.c., and run into a glass tube in which is also the drop of blood, which floats on the surface in globules. (*b*) is now added until the globules of blood show no tendency to rise or sink; the sp. gr. of liquid is then calculated, and a correction made for temperatures other than 15·6 (60° F.), namely, 0·88 sp. gr. for every 2° above 60° F.
E. W. P.

The Blood in Leucocythæmia. By E. FREUND and F. OBERMAYER (*Zeit. physiol. Chem.*, **15**, 310—318).—A large quantity of blood was obtained from a large hæmatoma occurring in a case of leucæmia. The amount of hæmoglobin in it was 25 per cent. of the normal; the number of red corpuscles was a little over a million per cubic millimetre, instead of the normal five millions, and the white corpuscles were nearly as numerous (945000). The general analysis may be usefully contrasted with other analyses in the following table:—

In 1000 *parts of Blood.*

	Present case.	Normal. C. Schmidt.	Normal. Becquerel and Rodier.	Chyluria. Hoppe-Seyler.	Sarcoma. Hoppe-Seyler (this vol., p. 481).
Water	895·8	788·71	779·0	796·78	793·36
Solids	104·2	211·29	221·0	203·22	206·64
Proteïds and hæmatin	72·0	—	—	—	—
Proteïds	—	—	76·0	33·54	59·16
Fibrin	—	3·93	2·2	—	-
Proteïds and extractives	—	192·10	—	—	—
Peptone	12·3	—	—	—	—
Hæmoglobin	—	7·38	134·5	149·6	129·70
Fat	7·1	—	1·60	1·7	2·31
Lecithin	3·8	—		3·48	2·01
Cholesterol	2·1	—		1·58	2·26
Extractives and salts	—	—	6·80	—	—
Salts	9·8	7·88	—	6·98	5·01

The most striking points about leucæmic blood are these: a low percentage of solids, the high percentage of fatty substance, and the presence of peptone, which has, however, been previously described in this disease by Bockendal and Landwehr (*Virch. Arch.*, **84**, 561). Several other tables are given to illustrate minor points of composition, but the two following, which appear to be the most important, may be quoted.

100 *parts of Solids contain.*

	Present case.	Chyluria (Hoppe-Seyler).	Melanotic sarcoma (Hoppe-Seyler).
Fat...................	6·81	0·83	1·11
Lecithin	2·74	1·71	0·99
Cholesterol	2·01	0·77	1·09

The ash shows an excess of phosphoric anhydride as compared with normal blood; two other analyses are here also given, one a case of mastitis, the other of empyema.

	Present cases.			Normal (Jarisch, *Med. Jahrb.* 1877, Heft 1).
	Leucæmia.	Mastitis.	Empyema.	
P_2O_5	16·92	24·12	13·21	8·82
SO_3	12·31	4·27	3·33	7·11
Cl	17·82	20·09	34·07	30·74
K_2O	15·65	3·64	3·08	26·55
Na_2O...........	38·52	40·46	43·69	24·11
CaO	0·47			0·90
MgO	0·07	5·49	5·53	0·53
Fe_2O_3	2·24	(as phosphates)	(as phosphates)	8·16
	104·00	—	—	106·92
Subtract oxygen for chlorine........	4·00	—	—	6·92
Total............	100·00	—	—	100·00

W. D. H.

Formation of Lactic Acid and Glucose in the Organism. By T. Araki (*Zeit. physiol. Chem.*, **15**, 335—370).—Lactic acid has been shown to be one result of activity or death in various active tissues, and occurs in the urine in phosphorus poisoning, and after extirpation of the liver. In the present research, the influence of diminishing the supply of atmospheric oxygen on the urine was considered. The lactic acid was estimated in the ethereal extract as the zinc salt. Preliminary experiments with muscular tissue showed that Hoppe-Seyler's, and also Werther and Drechsel's modifications (*Pflüger's Archiv*, **46**, 68) are both good methods yielding a zinc salt free from potassium chloride.

A series of experiments on dogs (which were supplied with less oxygen than there is in the atmosphere by the use of an apparatus constructed on the Regnault principle) gave the following results :—

the urine was always acid, contained lactic acid (the quantity of zinc lactate being generally less than 0·5 per cent.), generally gave the tests for sugar and albumin readily; if, however, the animals were in a condition of inanition, the urine yielded lactic acid and albumin, but no sugar. Experiments with hens gave corresponding results.

The same results followed poisoning by carbonic oxide, curare, and strychnine; and also after epileptic seizures, where the respiration is greatly retarded. Diminution of oxidation in the body is a factor common in all these conditions, and is doubtless a primary cause of the abnormal metabolism. W. D. H.

Lactic Acid and Glucose in Organs with Impeded Circulation, and in Hydrocyanic Acid Poisoning. By H. ZILLESSEN (*Zeit. physiol. Chem.*, **15**, 387—404).—From experiments on dogs and rabbits, the following conclusions are drawn:—

1. By artificially diminishing the amount of oxygen supplied to the muscles and liver during life (this was done by ligaturing the arteries supplying the parts in question), lactic acid is formed in those organs in increased amount.

2. In poisoning by hydrocyanic acid, lactic acid passes into the blood, diminishing its normal alkalinity. The amount of sugar in the blood is also increased.

3. Bernard and Preyer pointed out that when frogs are poisoned with hydrocyanic acid, the venous blood becomes of a bright, cherry-red colour, but in mammals this appearance very soon fades away. The cause of this change of colour is not known, but in the present research, the difference between cold and warm blooded animals is shown to be simply a matter of body temperature; a frog kept at a mammal's temperature in a warm bath behaving in this respect just like a mammal. W. D. H.

Chemical Composition of the Notochord. By A. KOSSEL (*Zeit. physiol. Chem.*, **15**, 331—334).—A considerable quantity of the material of which the notochord is constructed was obtained from large lampreys. Stenberg (*Du Bois Reymond's Arch.*, *Anat. Abth.*, 1881, 105) states that neither gelatin nor chondrin is obtainable from the notochord; and Neumann (*Ard. Mikr. Anat.*, **14**, 54) states that the cells stain with iodine as though they contained glycogen.

The notochord in the present research was found to contain from 95 to 96 per cent. of water; this contrasts very forcibly with cartilaginous tissue, and corresponds to what one would expect in an embryonic structure. The amount of ash present was 0·85 per cent. (0·805 soluble, and 0·047 insoluble, salts). The amount of glycogen present constituted 12 to 15 per cent. of the solids present. There was not much more than a trace of proteïd matter soluble in water. Gelatin, collagen, and mucin were all absent; and the bulk of the solid matter was an insoluble proteïd, easily digested by artificial gastric juice, and yielding no reducing sugar on treatment with mineral acids. W. D. H.

Mucoïd Substance in Ascitic Fluid. By O. HAMMARSTEN (*Zeit. physiol. Chem.*, **15**, 202—207).—Only a few observations of mucoïd material (paralbumin and metalbumin, or pseudomucin) occurring in ascitic fluid have been previously published. The present communication relates to six such cases. No. 1 occurred in a man, aged 66, suffering from cirrhosis of the liver. The fluid (sp. gr. 1·012) was alkaline, greenish, and opalescent; the opalescence remained after the separation of fibrin by spontaneous coagulation. Acetic acid gave no precipitate. By dialysing into water, the fluid became cloudy from precipitation of globulin; the fluid also gave Trommer's test (produced not by glucose, but by some unfermentable substance); the proteïd in the fluid yielded, after treatment with boiling mineral acid, a reducing substance in the same way as does mucoïd. The latter substance was isolated in the following way:—The fluid was acidified and boiled, the resulting coagulum was filtered off, and the filtrate concentrated on the water-bath, alcohol being added, and the precipitate which formed was collected; this was dissolved in water and again precipitated by alcohol, again dissolved in water, and dialysed to get rid of adherent sodium chloride. To the filtered liquid acetic acid was added, and the result was a white, flocculent precipitate nearly insoluble in excess of the acid. It was dissolved in a weak alkali, reprecipitated by acetic acid, and washed with water, alcohol, and ether. The filtrate, from which the precipitated mucoïd had been separated, gave a further precipitate with alcohol, which was purified by repeated solution and reprecipitation. It also belonged to the mucin group of substances, and was found to be similar in its reactions to an albumose formed by the action of alkali on mucin, and is termed *mucin-albumose*.

Mucoïd is insoluble in water, but soluble in feebly alkaline or acid liquids, which solutions remain clear on boiling. It gives Heller's test and the xanthoproteïc reaction. It is precipitated by acetic acid; it is soluble in great excess of this acid, and again becomes cloudy on the addition of potassium ferrocyanide, or of tannic acid, but not of sodium acetate. Hydrochloric acid gives a precipitate readily soluble in excess. Mercuric chloride gives no precipitate. Potassio-mercuric iodide with hydrochloric acid gives a precipitate, but copper sulphate produces only a cloudiness.

The substance, moreover, gives Millon's, the Adamkiewicz, and the biuret colour reactions. On boiling with copper sulphate and potassium hydroxide, no reduction occurs; but if the mucoïd has previously been heated with 2 per cent. hydrochloric acid on the water-bath, it then readily gives Trommer's test. Mucoïd contains 51·4 carbon, 6·8 hydrogen, and 13·01 nitrogen, per cent. It also contains sulphur.

Mucin-albumose is easily soluble in water. This solution is not changed by boiling. Acetic acid, with or without potassium ferrocyanide, and hydrochloric acid give no precipitate. It is precipitated by nitric acid, but not by tannic acid, unless acetic acid be added as well. Various salts of the heavy metals give either no precipitate, or only an opalescence. The substance gives the xanthoproteïc, Millon's, the Adamkiewicz, and the biuret colour tests. It does not give

Trommer's test unless it is previously boiled with dilute hydrochloric acid. It is precipitated by saturating its solution with ammonium sulphate, but not by sodium chloride. It contains 49·79 carbon, 6·96 hydrogen, and 11·42 nitrogen per cent. It also contains sulphur.

These two substances are considered to be derived from a more complex mother substance of proteïd nature pre-existent in the fluid.

Analysis of the fluid led to the following result; the numbers are percentages:—Water, 96·847; solids, 3·153; proteïd, 1·917; mucoïd substance, 0·118; salts, 0·866.

The other five cases gave very similar results. The following further elementary analyses may be quoted:—

Case 2.—Mucoïd, N, 13·1 per cent.; mucin albumose, C, 49·87; H, 6·88; N, 11·4.

Case 3.—Mucoïd, N, 12·4; mucin albumose, N, 10·8.

Case 4.—Mucin albumose, N, 11·37.

Concerning the significance of the appearance of mucoïd substances in ascitic fluid, it is at present premature to speak. W. D. H.

Excretion of Iron. By R. Gottlieb (*Zeit. physiol. Chem.*, **15**, 371—386).—The question of the absorption of iron salt is of high importance, but still involved in obscurity; one of the difficulties in the way is the want of knowledge concerning the excretion of iron. Very little passes away by the urine, even after intravenous or subcutaneous injections of neutral iron-containing compounds. Observers differ as to whether it passes away with the bile or not. Buckheim and Mayer (*Inaug. Diss. Dorpat*, 1850) believe that not only the bile, but the whole intestinal mucous membrane, takes part in the excretion. Quincke (*Du Bois Reymond's Archiv*, 1868, 150) could, however, find none of the metal in a Thiry's intestinal fistula. Previous observations have been, however, merely qualitative. In the present research quantitative analyses were made for the first time. Dogs were used for the investigation, and the salt injected was the double tartrate of iron and sodium, dissolved in a feebly alkaline solution.

100 milligrams of iron were subcutaneously injected during four days. During this time, and 24 days following, the fæces contained a total of 96·9 milligrams of iron in excess of that found there before the injection was made. In other words, practically the whole of the iron passed into the intestinal canal. Several experiments were then made in which the metallic compound was injected intravenously; about 70 per cent. of the metal was ultimately found in the intestine. After protracted injections, the greatest part of the metal left in the body was found in the liver. Other metals, like copper and magnesium, behave similarly. The question arises, how does the iron ultimately reach the intestine from the liver? Apparently it is not by the bile, but by the circulating blood, the iron being in the end removed from the blood by the intestinal epithelium, and excreted into the intestine. W. D. H.

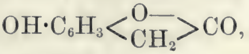
Alcaptonuria. By M. Wolkow and E. Baumann (*Zeit. physiol. Chem.*, **15**, 228—285).—The word alcapton was originally used by

Bödeker (*Zeit. rat. Med.*, **7**, 130) for a nitrogenous reducing substance occurring in certain urines, which became brown on the addition of an alkali in the presence of oxygen. Similar cases were described by Ebstein and Müller (*Virchow's Arch.*, **62**, 554), and Fleischer (*Berlin. klin. Woch.*, 1875, Nos. 39 and 40). Fürbringer (*ibid.*, No. 28) first advanced the theory that alcapton was not nitrogenous, but was identical with catechol, a view which, until recently, was generally accepted. W. Smith (*Dublin J. Med. Science*, 1882, 465) showed, however, that in one case protocatechuic acid, and not catechol, was the substance in question, and Kirk (Abstr., 1890, 188) has in another series of cases described a new acid which he terms uroleucic acid. Marshall (*Amer. J. Pharm.*, 1887, 131) describes a very similar acid as glycosuric acid. In all these cases, however, alcaptonuria does not appear to be pathological, but rather evidence of the presence of an idiosyncrasy in metabolism lasting throughout, or during long periods of otherwise healthy life.

In the present case, the questionable material was obtained from the greatly concentrated urine by rendering it strongly acid, and shaking it with ether. From the ethereal solution, it was obtained by evaporating off the ether, taking up with water, and precipitating by lead acetate; the lead was removed from the precipitate by hydrogen sulphide. The acid was once more extracted with ether, which on evaporation yielded crystals. These consisted of a substance very similar to, but not identical with, Kirk's uroleucic acid, and the name *homogentisic acid* is given to it. Analysis of the dried crystals correspond very well with the formula $C_8H_8O_4$. It reduces alkaline cupric salts and silver salts readily, but bismuth salts with great difficulty. With Millon's reagent, it gives a yellow coloration which turns red on boiling. It is monobasic, and contains two phenolic hydroxyl groups, but it is not identical with any of the hitherto described 16 acids with the same formula. It melts at 146·5—147°. *Lead homogentisate*, $(C_8H_7O_4)_2Pb + 3H_2O$, crystallises in colourless, brilliant, transparent needles and prisms. Its melting point is 214—215°. It dissolves in 675 parts of water at 20°, and is insoluble in alcohol and in ether. *Ethyl homogentisate*, $C_8H_7O_4Et$, is formed by passing hydrogen chloride through an alcoholic solution of the acid, diluting with water after 24 hours, adding excess of sodium hydroxide, and then shaking with ether. Its crystals are colourless prisms, soluble readily in hot, less readily in cold, water, readily soluble in alcohol and ether, but with difficulty in chloroform and benzene; they melt at 119—120°. The *methyl* salt crystallises in clinorhombic plates and melts at 45°.

Dimethylhomogentisic acid, $C_8H_6O_4Me_2$, melting at 124·5°, was also prepared.

By fusing homogentisic acid with alkali, short, colourless prisms melting at 196—198°, and with all the properties of gentisic acid, were obtained.

By heating the acid for a short time above its melting point, it is changed into its *lactone*,  $\mathrm{OH{\cdot}C_6H_3}\left<\begin{matrix}\mathrm{O—}\\ \mathrm{CH_2}\end{matrix}\right>\mathrm{CO}$, which forms short, prismatic crystals and melts at 191°.

From these and similar considerations, homogentisic acid is believed to be quinol, in which one hydrogen is replaced by an acetic acid residue, $C_6H_3(OH)_2\cdot CH_2\cdot COOH$ $[(OH)_2 : CH_2 = 1 : 4 : 3]$. Kirk's uroleucic acid is trihydroxyphenylpropionic acid; the present acid is dihydroxyphenylacetic acid.

Further researches showed that the excretion of sulphates (preformed and combined) in the urine remains normal. A method is also given by which the new acid can be estimated in the urine, by means of its reducing action on silver salts.

Theoretical considerations lead to the conclusion that the proteïds of the body form the source of the acid, and further, that tyrosine is an intermediate product in this metabolism. When dogs are fed upon it, it is split up into carbonic anhydride and toluquinol.

W. D. H.

Proteïd in Normal Urine. By H. WINTERNITZ (*Zeit. physiol. Chem.*, **15**, 189—201).—Senator states that normal urine always contains a trace of proteïd matter, but distinguishes between this and physiological albuminuria. Posner (*Berlin. klin. Woch.*, No. 41) also states that a trace of albuminous material can always be obtained from normal urine. The urine was carefully filtered and concentrated; the proteïd tests employed were Heller's nitric acid test and the acetic acid and potassium ferrocyanide reaction. The present research is mainly a repetition of Posner's work; larger quantities of urine were, however, employed, and in only one case was the precipitate produced by acetic acid and potassium ferrocyanide found to contain proteïd. The general conclusion drawn, which coincides with that of Leube (*Zeit. klin. Med.*, **13**, Heft 1), is that normal urine seldom contains even a trace of proteïd. W. D. H.

Hæmatoporphyrin in Urine. By E. SALKOWSKI (*Zeit. physiol. Chem.*, **15**, 286—309).—A full communication on a subject concerning which a preliminary account has already appeared (this vol., p. 601).

W. D. H.

Physiological Action of Nickel-Carbon Oxide. By J. G. MCKENDRICK and W. SNODGRASS (*Brit. Med. J.*, i, 1891, 1215—1217). —This compound, $Ni(CO)_4$ (Mond, Langer, and Quincke, Trans., 1890, 749), is a powerful poison when injected into animals subcutaneously; its vapour even to the extent of 0·5 per cent. in air is dangerous. The symptoms are those of respiratory poisoning, and are similar to those caused by carbonic oxide. The spectrum of the blood of an animal poisoned in this way is that of carbonic oxide hæmoglobin. When the substance is injected subcutaneously, it is probably in part dissociated in the tissues; there is evidence of the presence of nickel in the tissues and also in the blood. The substance produces a remarkably prolonged fall of body temperature, probably by interfering with respiratory processes. Its poisonous qualities are, however, at present a bar to its clinical use as an antipyretic.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Osmotic Experiments on Living Bacteria. By A. WLADIMIROFF (*Zeit. physikal. Chem.*, **7**, 529—543).—As De Vries investigated the phenomena of osmotic equilibrium between living plant cells and various salt solutions, so the author has undertaken an analogous research with living bacteria. The method adopted was to examine the movements of the bacteria in a drop of salt solution and meat broth hanging from the cover-glass of a suitable microscopic slide, and to observe at what concentration there remained a few bacteria which retained the ability to swim slowly, and in what slightly stronger solution the last swimming bacterium had vanished. The mean of these concentrations gives what the author terms the "limiting solution," which he has determined for various organisms and a considerable number of salts. From the numerical results he concludes that in the majority of cases the relations between salts and bacteria obey the laws of osmosis (osmotic pressure). Some neutral salts, however, seem to have a poisonous effect on certain bacteria, whilst others appear to be able to penetrate the protoplasm of particular organisms, both of these being disturbing elements in the study of the purely osmotic phenomena.

The following table gives the limiting solutions in gram-molecules per litre :—

	Bacterium Zopfii.	*Bacillus cyanogenus.*	*Bacillus typhi.*	*Bacillus subtilis.*	*Spirillum rubrum.*	Intestinal bacterium.
KCl	0·358	0·728	0·728	0·651	0·755	0·720
NaCl	0·316	0·656	0·597	0·450	0·635	0·635
NH_4Cl ...	0·312	0·624	0·580	0·422	0·552	0·430
KNO_3	0·318	0·635	0·611	0·616	0·668	0·714
$NaNO_3$ ...	0·277	0·474	0·468	0·507	0·597	0·627
NH_4NO_3 ..	0·222	0·512	0·510	0·340	0·512	0·394
KBr	0·204	0·626	0·491	0·450	0·537	0·493
NaBr	0·192	0·597	0·460	0·422	0·518	0·554
K_2SO_4	0·286	0·488	0·478	0·295	0·436	0·328
Na_2SO_4 ...	0·280	0·474	0·482	0·277	0·435	0·306

A corresponding table may be made to express the behaviour of the salts towards the protoplasm :—

	Bacterium Zopfii.	*Bacillus cyanogenus.*	*Bacillus typhi.*	*Bacillus subtilis.*	*Spirillum rubrum.*	Intestinal bacterium.
KCl	perm.	perm.	perm.	perm.	perm.	perm.
$NaCl$	imperm.	imperm.	imperm.	imperm.	imperm.	—
NH_4Cl....	"	"	"	"	"	—
KNO_3	"	"	"	perm.	perm.	perm.
$NaNO_3$ ...	—	poison	poison?	perm.?	imperm.	—
NH_4NO_3..	poison	"	—	poison	"	—
KBr......	"	imperm.	poison	imperm.	"	—
$NaBr$	"	"	"	"	"	—
K_2SO_4....	imperm.	"	imperm.	poison	"	—
Na_2SO_4 ...	"	"	"	"	"	—

J. W.

Secretions of Microbes: Transformation and Elimination of Nitrogenous Organic Matter by the Pyocyanic Bacillus in a given Cultivation Medium. By A. ARNAUD and A. CHARRIN (*Compt. rend.*, **112**, 755—758).—The fluid in which *Bacillus pyocyanicus* was allowed to develop contained per litre 5 grams of asparagine, 0·100 gram of dipotassium phosphate, 0·100 gram of crystallised disodium phosphate, 0·134 gram of potassium hydrogen carbonate, 0·050 gram of calcium chloride, and 0·050 gram of crystallised magnesium sulphate. The liquid after inoculation was kept at 25—30°, and the blue colour appeared after about 24 hours, but the quantity of pyocyanin formed is not proportional to the general activity of the bacillus. The asparagine disappears after about 60 hours; aspartic acid is formed from the beginning but afterwards is destroyed, the decomposition being complete after about 72 hours. At this time the whole of the nitrogen has been converted into ammonia, with the exception of the small quantity that has gone to form the protoplasm of the microbes, and a small quantity that has been converted into compounds not yet defined. The weight of the microbes varies with the age of the cultivation. When the proportion of asparagine is varied the same products are obtained in the same times in absolutely the same proportions.

The bacillus splits up the asparagine by means of a diastase. The filtered liquid has no action on the asparagine *in vitro*, but if the bacilli are washed and transferred to an asparagine solution containing chloroform to prevent vital action, the asparagine is converted into aspartic acid.

C. H. B.

Assimilation by Lichens. By H. JUMELLE (*Compt. rend.*, **112**, 888—891).—Under favourable conditions of light, humidity, and season, all lichens can decompose the carbonic anhydride of the air so energetically that the quantity decomposed exceeds that evolved from the lichen by the process of respiration, and consequently the organism gains in carbon. The intensity of the assimilation of lichens varies enormously, however, with the species, and is relatively strong with lichens such as *Cladonia* or *Parmelia*, but is very feeble in the case of crustaceous lichens such as the *Lecidea*. Other conditions remaining the same, direct sunlight is more favourable to assimilation than diffused light. C. H. B.

Influence of Salt on the Quantity of Starch contained in the Vegetating Organs of Lepidium sativum. By P. LESAGE (*Compt. rend.*, **112**, 891—893).—The plants were watered with solutions containing from 1 to 25 grams of salt per litre, or, in a second series 4 to 100 per cent. of sea water. With 12 to 15 grams of salt per litre, starch disappears completely from every part of the plant. The disappearance of the starch, however, is not directly proportional to the quantity of salt present in the water. In both series there is a minimum in the leaves and root when the water contains 1·66 grams of salt per litre or 6·7 per cent. of sea water, and with stronger solutions the quantity of starch again increases, until with the amount already stated it disappears altogether. It is not improbable that the real maximum is obtained by watering with solutions containing a quantity of salt between 0·0 and 1·66 grams per litre. C. H. B.

Dextrose from Ipecacuanha Root. By E. MERCK (*Arch. Pharm.*, **229**, 169—170).—When preparing emetine from ipecacuanha root, about 5 per cent. of a compound identical with dextrose was obtained. This compound does not appear to exist in all varieties of the root, as no sugar could be detected in samples from other sources. J. T.

Macassar Oil. By K. THÜMMEL and W. KWASNIK (*Arch. Pharm.*, **229**, 182—197).—Macassar oil is obtained from the seed of *Schleichera trijuga*, Willd., *Cussambium spinosum*, an East Indian tree of the order Sapindaceæ. The oil can be obtained from the seed either by pressure or by treatment with light petroleum. The brown scale of the seeds amounts to 45 per cent., whilst the cotyledon containing the oil is 55 per cent. The cotyledons yield 68 per cent. of fatty oil by pressure, yellowish in colour, of the consistency of soft butter. The oil is composed of glycerides of acetic, oleïc, palmitic, and arachidic acids. The fatty acids are present in the relative proportion of oleïc acid 70 per cent., palmitic 5 per cent., and arachidic 25 per cent. It also contains free hydrocyanic acid and other volatile acids (formic, acetic acid). J. T.

Constituents of Rhizoma podophylli. By R. KÜRSTEN (*Arch. Pharm.*, **229**, 220—248).—The results of the present investigation supplement the work done by Podwyssotzki (Abstr., 1882, 976). The podophyllotoxin prepared by Podwyssotzki's method was not constant in composition, and its melting point varied from 100° to 125°: further, the podophyllic acid of that author is composed mainly of a crystallisable, active, but very impure substance. Podophyllotoxin, $C_{23}H_{24}O_9 + 2H_2O$, is obtained by extracting the coarsely powdered rhizome with cold light petroleum, until freed from fat; after drying in the air, the extraction is continued with chloroform, until the liquid comes away almost free from yellow colour. As it is not possible to work with alcohol-free chloroform, too prolonged extraction with chloroform would yield a more impure extract. The chloroform extract is distilled, and the residue is dried over a not too warm water-bath, partially dissolved in benzene, filtered, and the filtrate allowed to remain from 3 to 8 days, when a brownish-yellow mass of well formed, thick, strongly refractive prisms is produced, which is purified by washing with 50 per cent. alcohol, then with ether, recrystallising first from boiling benzene, and finally from solution in hot 45 per cent. alcohol. The compound is thus obtained in long, well-formed prisms. It melts at 93—95°, and at a higher temperature chars without subliming. 100 c.c. of water at 15° dissolves 0·014 gram; hot water dissolves somewhat more. It is very slightly soluble in ether and cold benzene, easily soluble in acetone and strong alcohol, and with difficulty in concentrated acetic acid. When moistened with concentrated sulphuric acid the crystals give an immediate cherry-red coloration, which slowly passes through greenish-blue to violet. Concentrated hydrochloric and nitric acids produce a red coloration; ferric chloride and bromine produce no change; the compound dissolved in glacial acetic acid gives a red coloration with Millon's reagent. The alcoholic solution is strongly lævorotatory. Zeisel's method indicates the presence of three methoxyl groups. Hydroxyl does not appear to be present.

Podophyllotoxin, when oxidised in an alkaline solution in the cold, by means of potassium permanganate, yielded, besides a little carbonic anhydride and a brown, amorphous substance, principally two compounds, the more considerable of which was *podophyllic acid*, $C_{20}H_{24}O_9$, obtained as well-formed, colourless crystals, from solution in a mixture of benzene and alcohol. The compound is without action on animals. It melts at 158—160°. Its aqueous solution, neutralised with aqueous potash, gives no precipitate with gold, calcium, or barium chlorides; silver nitrate gives a white precipitate, soluble in much water; copper acetate gives a blue precipitate. The *copper* salt, $(C_{20}H_{23}O_9)Cu$, was prepared as beautiful, light-green prisms, and analysed.

Picropodophyllin results from the action of alkalis on podophyllotoxin; thus, on heating the latter with aqueous ammonia, a well crystallised product is obtained, which at first was recrystallised from strong alcohol; but this was found to be unnecessary, as the melting point, 227°, was not affected by it. Picropodophyllin has the same composition as podophyllotoxin, but they differ in melting point: 227° and 95°; in their action on polarised light: inactive, lævorotatory; as to solubility, the former is less soluble in all liquids than the latter; the latter gives Millon's reaction, the former does not. By oxidation and reduction the two compounds yield the same products. The residue of the chloroform extract, freed from crystalline podophyllotoxin, yielded a little *picropodophyllic acid* in crystals melting at 156—158°; no other definite substance could be obtained from the extract.

Podophylloquercetin, $C_{23}H_{16}O_{10}$, is best obtained from the rhizome, after extraction by light petroleum and chloroform, by further extracting with ether, distilling off the ether, and treating with cold glacial acetic acid. The crude crystals are purified by repeated recrystallisation, best in an atmosphere of carbonic anhydride. It melts at 275—277°, is almost insoluble in water, sparingly soluble in cold glacial acetic acid, more soluble in the hot acid and in ether, easily soluble in strong alcohol. Alkaline copper solution is easily reduced when warm, also ammoniacal silver solution. Probably this compound is not identical with quercetin. J. T.

Decomposition of the Silicates in Soil by Lime and Gypsum. By G. DE MARNEFFE (*Bied. Centr.*, 1891, 294—296).—Three classes of soils were ignited and extracted with dilute hydrochloric acid to remove all soluble silicates. They were then mixed with lime, some being exposed to air; others were kept air-tight, but water was given in all cases. The result was that insoluble silicates were rendered soluble, but the presence or absence of air made no difference. Another set of samples were treated in like manner, but mixed with gypsum; this addition produced no change in composition. E. W. P.

Value of Nitrates and Ammonium Salts as Food for Ferments and other Plants. By E. LAURENT (*Bied. Centr.*, 1891, 358—359).—Ammonium sulphate and phosphate, potassium and sodium nitrates, and also potassium nitrite, were applied to plants. The last compound is poisonous, and so is ammonium nitrate, if the solution be acid, for the ferment reduces nitrate to nitrite. Several mildews prefer ammonium salts to nitrates. With green plants in water culture, it was found that the roots of the "ammonia plants" ramify more in solutions of ammonium salts, but, on the other hand, the roots are shorter than when in solutions of nitrates. When grown in soil, plants fed with nitrates do best. E. W. P.

Characteristic of Fig Wine. By P. CARLES (*Compt. rend.*, **112**, 811—812).—Figs, when moistened with tepid water acidified with tartaric acid, rapidly ferment, and yield a wine of about 8° alcoholic strength and very free from acidity. This wine is largely made in Algeria, although the figs from Asia Minor give the best results; it is used for adulterating grape wines, and also for defrauding the revenue.

If the fig wine is evaporated to a syrup, and left in a cool, dry place, it does not remain liquid, but after 24 hours solidifies to a crystalline mass, consisting chiefly of mannitol, together with glycerol, and a small quantity of sugar and organic acids. The proportion of mannitol amounts to from 6 to 8 grams per litre, whilst in the ordinary wines it does not exceed a few decigrams per litre. Estimation of the mannitol, therefore, makes it possible to detect the addition of as little as 25 per cent. of fig wine to ordinary wine.

C. H. B.

Analytical Chemistry.

Measurement of Gases. By G. LUNGE (*Ber.*, **24**, 1656—1657).—A criticism of a recent paper of F. R. Japp on this subject (compare Proceedings, 1891, 68).

Estimation of Small Quantities of Alkali and Recognition of the Neutrality of Water. By F. Mylius and F. Foerster (*Ber.*, **24**, 1482—1498).—The authors' previous researches on the action of aqueous solutions on glass (Abstr., 1889, 828) were in many respects incomplete, owing to the fact that no alkalimetric method was known sufficiently delicate for those investigations. They have, therefore, endeavoured to obtain an indicator which would be sufficiently delicate to allow of the employment of millinormal solutions, and find that iodeosin answers the purpose admirably. The crude colouring matter must be purified by dissolving in aqueous ether, shaking the filtered solution with soda solution, and precipitating the sodium salt by the addition of concentrated soda solution. The salt is recrystallised from alcohol, dissolved in water, acidified with hydrochloric acid, and the precipitated iodeosin well washed with water. If used in the ordinary manner, this colouring matter is useless as an indicator, but if the titration is carried on in a stoppered bottle, in presence of ether, and the whole shaken on addition of the reagent, the point of neutrality is very distinctly shown, as in presence of the slightest excess of alkali the iodeosin passes from the aqueous to the ethereal solution, leaving the former almost colourless.

The titration with millinormal solutions allows of the detection of quantities of alkali equivalent to 0·1 milligram Na_2O, and even smaller amounts may be estimated by employing a colorimetric method. In carrying out the latter process a large number of precautions must be taken with regard to the neutrality of the water, the quality of the glass vessels employed, &c. For details of this method reference must be made to the original, as they do not admit of a curtailed description. H. G. C.

Estimation of Available Oxygen in Peroxides by Means of Gaseous Hydrochloric Acid. By L. L. de Koninck and A. Lecrenier (*Chem. News*, **63**, 280).—A modification of Bunsen's method. The oxide under examination is placed in a flask along with sufficient water to dissolve the chloride formed during the ensuing reaction, and, while gently heated, is submitted to the action of hydrogen chloride, conveyed in a current of carbonic anhydride; as soon as the oxide is dissolved, the supply of hydrogen chloride is stopped, but the current of carbonic anhydride is continued, and when the hydrogen chloride has been expelled, the liberated iodine in the receiver is titrated in the usual manner. D. A. L.

Estimation of Nitrate by the Phenolsulphonic Acid Method. By G. H. Bartram (*Chem. News*, **63**, 228—229).—Noting discrepancies in the results obtained in duplicate estimations of nitrates in water by the phenolsulphonic acid method, investigations were instituted which show that accurate results are obtained with freshly prepared phenolsulphonic acid, but that shortly after preparation, this reagent becomes susceptible to the action of chlorine when the quantity present is as much as, or more than four times, that of the nitric nitrogen, and the results may then be vitiated to the extent of showing a deficit of 20 or even 40 per cent. of the total nitric nitrogen actually present. This can, however, be obviated, either by removing the chlorides or by using freshly prepared phenolsulphonic acid. D. A. L.

Estimation of Sulphur. By F. P. TREADWELL (*Ber.*, **24**, 1937—1941).—The method is applicable to insoluble sulphides. It consists in heating the sulphide with excess of iron to dull redness in an atmosphere of dry carbonic anhydride for five to ten minutes, and after cooling, decomposing the iron sulphide with hydrochloric acid (1 : 5). The iron used is commercial ferrum reductum, and as this contains some sulphur, it is necessary to perform a blank experiment first. The hydrogen sulphide is absorbed in a Fresenius-Vollhard absorption apparatus; the first absorption bottle contains 50 c.c. of hydrogen peroxide solution (2 per cent.) and 10 c.c. of ammonia (2/1 N.), the second bottle contains 10 c.c. of the ammonia. After absorption of the hydrogen sulphide, the contents of the absorption apparatus are washed into a beaker, boiled for half an hour, acidified with hydrochloric acid, and evaporated to dryness on the water-bath. The dry mass is treated with a few drops of hydrochloric acid, dissolved in water, filtered, and the filtrate precipitated with barium chloride.

The results obtained compare very favourably with those obtained by other methods. E. C. R.

Estimation of Sulphur in Coal, &c. By T. NEILSON (*Chem. News*, **63**, 192).—The author has obtained satisfactory results by estimating sulphur in coal, &c., in the following manner:—A gram of coke mixed with 2 grams of sodium carbonate and half a gram of manganous carbonate is heated at a low red heat in a flat platinum dish for an hour, then fused, cooled, dissolved in hydrochloric acid, evaporated to dryness, redissolved in hydrochloric acid, filtered, and the sulphuric acid precipitated with barium chloride, &c., as usual. A blank experiment of equal duration should be made at the same time as the actual estimation. D. A. L.

Estimation of Barium as Sulphate. By F. W. MAR (*Amer. J. Sci.* [3], **41**, 288—295).—The author finds that in precipitating barium by means of sulphuric acid, it is highly advantageous to have the solution strongly acidified with hydrochloric acid, as the precipitate is then formed in a more or less crystalline condition, settles rapidly, and can be safely filtered with or without pressure in ten minutes. It is not necessary to add the reagents drop by drop, but the whole quantity required to complete the reaction may be added at once. Ordinary quantities of barium salts, in presence of a considerable excess of sulphuric and hydrochloric acids are precipitated completely and at once, but when only a few milligrams are present, the precipitate requires more time, usually from two to three hours, to separate under the same conditions. If sulphuric acid is being estimated by means of barium in the presence of alkali salts, the barium sulphate can be purified by dissolution in concentrated sulphuric acid and subsequent evaporation to dryness, when the sulphate is left in large crystals, which can be filtered off as readily as sand. This is far better than the old method of solution and reprecipitation by dilution.

H. C.

Separation of Cadmium and Copper. By H. N. WARREN (*Chem. News*, **63**, 193).—Copper is completely precipitated from its solutions by glucose in the presence of Fehling's tartrate solution, and may be readily and efficiently separated from zinc and cadmium by dissolving the alloy containing the three metals in nitric acid, diluting, mixing with excess of Rochelle salt and sufficient sodium hydroxide, then adding a dilute solution of glucose in quantities of not more than 4 c.c. at a time to the clear boiling solution.

D. A. L.

Precipitation of Manganese as Ammonium Manganous Phosphate. By A. G. MCKENNA (*Chem. News*, **63**, 184—186; from *Tech. Quarterly*, **3**, No. 4).—The author shows that glass vessels may be used for the precipitation of ammonium manganous phosphate from the solution of the chloride; that in several experiments boiling in the beaker has been continued, with constant stirring, until the precipitate assumed a silky appearance, some eight minutes, without getting silica from the glass. It is shown to be important that the precipitate be obtained crystalline; experimental data indicate that the ammonium manganous phosphate is only very slightly soluble either in hot water, aqueous ammonia (1 : 4), or ammonium nitrate, but least of all in the first, which, moreover, does not affect its appearance; the author, therefore, washed the precipitate with hot water. In the presence of iron, a manganese compound is formed, which is soluble in ammonia when an excess of an alkaline phosphate is not present.

D. A. L.

Alcohol Method for Estimating Iron and Aluminium Oxides in Phosphates. By H. H. B. SHEPHERD (*Chem. News*, **63**, 251).—This method, modified to meet objections raised at meetings called by the Chemical Manure Manufacturers' Association, is conducted in the following manner:—$2\frac{1}{2}$ grams of phosphate is dissolved in 10 c.c. of hydrochloric acid, evaporated to dryness, redissolved in hydrochloric acid, heated to boiling, washed with as little water as possible, into a 250 c.c. flask, where it is mixed with 10 c.c. of strong sulphuric acid, and agitated frequently during five minutes. Alcohol (95 per cent.) is now added, the mixture is cooled, made up to the mark with alcohol, and well shaken; as contraction occurs on mixing, it must again be made up to 250 c.c. After an hour, 200 c.c. of the filtered solution is gently evaporated to a small bulk or to a paste if organic matter is present, mixed with 50 or 100 c.c. of water and boiled for a short time with bromine or other oxidising agent. Ammonia is now added in excess, the whole boiled for half an hour, cooled, a little more ammonia added, the precipitate of the phosphates of iron and alumina collected, washed with a hot solution of ammonium chloride, ignited, and weighed. The phosphoric acid is determined in the precipitate, and its weight deducted; the iron may also be determined if desired. Teschemacher and Smith suggest that if any magnesia is present, it should be removed from the precipitate by boiling with water and a little ammonium nitrate, repeating the treatment if needful. D. A. L.

Separation of Iron from Cobalt and Nickel. By G. A. Le Roy (*Compt. rend.*, **112**, 722—723).—A solution containing iron, manganese, nickel, and cobalt in the form of sulphates is mixed with a large excess of a concentrated and strongly ammoniacal solution of ammonium sulphate, after addition of sufficient citric acid or other acid to prevent precipitation of the metals. The solution is then electrolysed with the current from two Bunsen cells (or their equivalent); manganese separates at the anode, and iron, nickel, and cobalt at the cathode. The cathode is washed, and is then put into a concentrated solution of ammonium sulphate saturated with ammonia. It now serves as the anode, a weighed platinum plate being the cathode, and when the circuit is closed, the nickel and cobalt are transferred to the new cathode, whilst ferric hydroxide partly remains on the anode and partly floats in the liquid, but is free from any appreciable traces of nickel or cobalt. C. H. B.

Separation and Estimation of Nickel and Cobalt. By C. Krauss (*Zeit. anal. Chem.*, **30**, 227—242).—The author has submitted to a critical study most of the hitherto published methods for separating nickel and cobalt. Many of them are entirely worthless. Fleischer's method (*Zeit. anal. Chem.*, **10**, 219) yields passable results, owing to a compensation of errors. Cobalt can be estimated by a modification of Donath's method (Abstr., 1880, 287; 1882, 555), in which the solution is boiled with potash and hydrogen peroxide, the cobalt peroxide then treated with potassium iodide, and the liberated iodine titrated. Rose's method, and those of Liebig, as well as Wöhler's, Rose's, and Gauhe's modifications of the latter, give satisfactory separation. Dirvel's method (Abstr., 1880, 287) yields satisfactory results if skilfully performed. Fischer's potassium nitrite method is serviceable, and that of Ilinski and Knorre (Abstr., 1885, 840) is excellent. M. J. S.

Precipitation of Antimony from Solutions of Potassium Antimony Tartarate. By J. H. Long and H. E. Sauer (*Chem. News*, **63**, 269—270).—By making the admixture slowly, and at a low temperature, an alkali carbonate may be added to a solution of potassium antimony tartrate, in quantities more than necessary for complete precipitation, without producing a precipitate; nevertheless, polarisation phenomena, inasmuch as the rotation is decreased, show that some chemical change has taken place; moreover, such solutions gradually became turbid, but without the evolution of carbonic anhydride, and, in time, deposit a precipitate. Series of experiments were instituted to investigate this matter. In one series, 5 grams of tartrate was dissolved in 60 to 70 c.c. of water cooled to 20°, to which was added a weighed amount of sodium carbonate dissolved in a little water; the mixture was diluted to 100 c.c. at 20° and left for 24 hours; with small amounts of carbonate, the precipitation was slow, but however small the precipitate, the supernatant liquid was always clear. Analyses of the precipitates in this series showed a mean of 78·8 per cent. of antimony; some of the results are as follows :—

Experiment.	Sodium carbonate added. grams.	Percentage of potassium antimony tartrate left in solution.
1	0·1	99·93
4	0·7	56·76
8	2·0	3·88

0·7982 gram of sodium carbonate should be sufficient to precipitate the 5 grams of tartrate present; the precipitation is evidently incomplete, but, nevertheless, in this series the amount of antimony retained in solution diminishes regularly as the quantity of sodium carbonate added increases. Other series of experiments, some mixed at 100°, others also kept at 100° for an hour, show an accelerated, but still incomplete precipitation; in fact, after a certain point when about 2 grams of sodium carbonate is added, the antimony in solution, having reached a minimum, begins to increase; this is still more evident when a greater dilution was employed. As the solution, then, has not the optical properties of the tartrate, and as it is influenced by an excess of sodium carbonate, it is presumed that the antimony may be present as antimonite, which probably is formed before a maximum in the oxide is reached. No evolution of carbonic anhydride took place in the cold or in the solutions simply mixed at 100°, but in the stronger solutions kept at 100° some carbonic anhydride was evolved. It seems that complete precipitation is only possible at very low temperatures. D. A. L.

Electrolysis of Metallic Phosphates in Acid Solution. By E. F. Smith (*Amer. Chem. J.*, **13**, 206—209; compare Abstr., 1890, 1028).—*Cadmium from Manganese.*—10 c.c. of cadmium sulphate solution (= 0·2399 gram of cadmium), 10 c.c. of manganese sulphate solution (= 0·1000 gram of manganese), 20 c.c. of disodium phosphate (sp. gr. 1·0358), 3 c.c. of phosphoric acid (sp. gr. 1·347), and 100 c.c. of water were electrolysed with a current liberating 10 c.c. of oxyhydrogen gas per minute. In 12 hours, 0·2394 gram of cadmium was precipitated. In trial No. 2, 0·2400 gram.

Platinum.—0·2590 gram of ammonioplatinic chloride (= 0·1144 gram of platinum); 30 c.c. of disodium phosphate; 5 c.c. of phosphoric acid; water to 150 c.c.; current = 0·8 c.c. of oxyhydrogen gas per minute for 10 hours; weight of platinum deposited, 0·1140 gram.

Palladium.—Palladium = 0·1825 gram; sodium diphosphate, 20 c.c.; phosphoric acid, 5 c.c.; water, 125 c.c.; current = 0·7 c.c. of oxyhydrogen gas per minute; weight of palladium deposited, 0·1817 gram. In second trial, 0·1830 gram. Palladium could not be separated from cadmium, zinc, and other metals.

Gold.—0·1338 gram of gold; 20 c.c. of disodium phosphate; 3 c.c. of phosphoric acid; water to 160 c.c.; current, 0·8 c.c. of gas per minute. The deposit was made on copper and weighed 0·1335 gram. In second trial, 0·1339 gram. Gold could not be separated from cadmium, but easily from zinc.

Gold from Zinc.—Gold, 0·1338 gram; zinc, 0·1500 gram; disodium phosphate, 30 c.c.; phosphoric acid, 3 c.c.; water to 150 c.c.; current, 0·6 c.c. of gas per minute; weight of gold deposited, 0·1338 gram.

Gold from Cobalt.—Conditions the same as those last mentioned, except for the presence of 0·2300 gram of cobalt; weight of gold deposited, 0·1338 gram.

Several details as to the condition of the deposited metals are given in the original. A. G. B.

Electrolytic Estimation of Rhodium. By A. JOLY and E. LEIDIÉ (*Compt. rend.*, **112**, 793—796).—Rhodium can be estimated with great accuracy by the electrolysis of solutions free from all other metals except the alkali metals. The solution of the chloride or double (sodium, potassium, or ammonium) chloride is slightly acidified and should not contain more than 4 grams of metal per litre. At the beginning, the liquid is heated to 50—60°, and a current of 0·5 ampère is used, but the operation is finished at the ordinary temperature with a current of 0·1 ampère. The method is applicable to any rhodium compound that can be converted into the chloride or a double chloride. If the separation is required and not the estimation, a stronger current may be used; the metal is then more crystalline and less coherent.

The metal can also be estimated in solutions of the sulphate, provided that the liquid contains a considerable quantity of free acid and the deposition is very slow.

Nitric acid, in quantity exceeding 20 per cent., prevents separation of the metal altogether, and with more than 10 per cent. deposition is very slow. In presence of oxalic acid, no rhodium separates at the cathode, but a dark-green peroxide separates at the anode.

C. H. B.

Volumetric Estimation of Volatile Hydrocarbons. By W. HEMPEL and L. M. DENNIS (*Ber.*, **24**, 1162—1164).—The authors describe a method of estimating the volatile hydrocarbons in gas. Only 100 c.c. of gas is employed for the determination. The method is based on Bunsen's, the hydrocarbons being absorbed by a small quantity of absolute alcohol. The gas is brought into an ordinary gas-burette and mixed with a small quantity of water saturated with gas. It is then transferred, by means of a capillary tube, to a gas pipette, containing 1 c.c. of absolute alcohol over mercury, and shaken three minutes. The alcohol must first be saturated with gas, to avoid any gas except the volatile hydrocarbons being absorbed. After shaking with alcohol, the gas is transferred back into the burette. To absorb alcohol vapours mixed with the gas, it is shaken in a pipette with 1 c.c. of water over mercury for three minutes and again transferred to the burette. The difference in volume gives the hydrocarbon vapours. The results are accurate.

Since the volatile hydrocarbons are appreciably soluble in caustic soda, in ordinary gas analysis the percentage of carbonic anhydride is too high. This error is easily avoided in the above method by determining the constituents in the following order: volatile hydrocarbons, carbonic anhydride, heavy hydrocarbons, oxygen, carbonic oxide, hydrogen, and marsh gas. E. C. R.

Gayon's Aldehyde Reaction. By H. Bornträger (*Zeit. anal. Chem.*, **30**, 208—209).—Gayon's reagent is a solution of rosaniline decolorised by a little hydrochloric acid and much sodium hydrogen sulphite. Its indications are untrustworthy, since many oxidising agents restore its red colour in the same way as aldehyde does. On the other hand, acetal destroys the rosaniline-red, and would therefore mask the aldehyde reaction. The reducing action of aldehyde on ammoniacal silver solution, and on ammoniacal permanganate, are the only certain tests at present known, but they both require the presence of a moderately large amount of aldehyde.

M. J. S.

Estimation of Acetone in Denaturised Alcohol. By L. Vignon (*Compt. rend.*, **112**, 873—875).—When iodine and sodium hydroxide act on acetone in presence of water, there are always two distinct reactions taking place simultaneously: (*a*) $COMe_2 + 3I_2 + 4NaOH = AcONa + CHI_3 + 3NaI + 3H_2O$, and (*b*) $3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O$, the one or the other predominating according to the conditions.

In presence of excess of methyl alcohol, the proportion of acetone amounting to 20 or 25 per cent., 13·7 atoms of iodine are required for the complete conversion of 1 mol. of acetone into iodoform, or 1 part of acetone requires 30 parts of iodine.

Ethyl alcohol alone yields no iodoform, but it greatly retards the conversion of acetone into iodoform, and tends to make the reaction (*b*) predominant. A mixture of acetone and water which yielded iodoform corresponding to 55·34 per cent. of acetone gave only 28·54 after dilution with an equal volume of ethyl alcohol, other conditions remaining the same. Aldehyde, on the other hand, promotes the formation of iodoform, and the preceding mixture, when an equal volume of aldehyde had been added, gave iodoform amounting to 95·93 per cent. of acetone.

It follows that in the estimation of acetone in denaturised alcohol by conversion into iodoform, a large excess of iodine must be used. 5 c.c. of the alcohol, after removal of the aldehyde by Bardy's method, is diluted to 250 c.c. with distilled water, and 5 c.c. of the solution (= 0·1 c.c. of the original alcohol) is mixed with 10 c.c. of binormal soda and 5 c.c. of binormal iodine. A second estimation is made with the same quantity of alcohol, but double the quantities of iodine and soda, and it is only when both experiments give the same result that the determination can be regarded as satisfactory.

C. H. B.

Use of Phenylhydrazine for the Estimation of Sugars. By Maquenne (*Compt. rend.*, **112**, 799—802).—The weight of the osazones precipitated when different reducing sugars are heated for the same time with the same weight of phenylhydrazine varies considerably with the nature of the sugar, but remains constant for the same sugar so long as the conditions are precisely the same. The following results were obtained by heating for an hour at 100° 1 gram of each sugar with 100 c.c. of water, and 5 c.c. of a solution containing 400 grams of phenylhydrazine and 400 grams of glacial acetic acid per litre; after cooling, the precipitate was collected, washed with

100 c.c. of water, and dried at 110°:—Sorbinose, 0·82; levulose, 0·70; xylose, 0·40; glucose (anhyd.), 0·32; arabinose, 0·27; galactose, 0·23; rhamnose, 0·15; lactose, 0·11; maltose, 0·11. With more dilute solutions, the relative differences remain practically the same, but levulose tends to approach sorbinose. It is noteworthy that sorbinose and levulose yield a much greater quantity of osazone in a given time than any other sugars, and these are the only two isomerides or homologues of glucose that have a ketonic function. The two are readily distinguished, since the glucosazone forms easily recognisable needles, whilst sorbinosazone never forms distinct crystals. Glucosazone and galactosazone, which both crystallise well and melt at practically the same temperature, can be distinguished by their rate of formation. It is also noteworthy that the reducing saccharoses give less osazone than the non-hydrolysable sugars, and therefore less than the products of their own inversion.

A comparison of the weight of osazone obtained from the products of inversion of polyglucoses with the weight obtained from a known mixture of glucoses affords valuable help in determining the products of inversion of the polyglucoses. The following results were obtained with 1 gram of sugar completely inverted by dilute sulphuric acid, dissolved in 100 c.c. of water and mixed with 2 grams of phenylhydrazine, 2 grams of glacial acetic acid, and 5 grams of sodium acetate; in each case the result is compared with that obtained with artificial mixtures of corresponding quantities of glucoses:—

	Weight of osazone.
Ordinary saccharose	0·71
Glucose and levulose (0·526 gram each)	0·73
Maltose	0·55
Glucose (1·052 gram)	0·58
Raffinose (cryst.)	0·48
Levulose, glucose, and galactose (0·303 gram each)	0·53
Lactose (cryst.)	0·38
Glucose and galactose (0·5 gram each)	0·39

The weight of osazone is always slightly lower in the case of the products of inversion, because of the destructive action of the acid. This error can be compensated by diluting the solutions until equal volumes have the same reducing power. In this way it was found that the product of the inversion of melezitose gives the same weight of osazone as a solution of glucose of equal reducing power, and therefore glucose is the sole product of the inversion of melezitose.

C. H. B.

Saponification by means of Sodium Ethoxide. By A. Kossel and M. Krüger (*Zeit. physiol. Chem.*, **15**, 321—330).—The method of saponification introduced by Kossel and Obermüller (Abstr., 1890, 1474) is shown to be applicable to the analysis of butter and suet.

Practically identical results were obtained, whether the analysis was performed by the new method or by the alcoholic potassium hydroxide method.

In the saponification of cetyl palmitate by the new method, one product is sodium palmitate, the other is cetyl alcohol. In the saponification of phenyl salicylate (salol), one product is ethyl salicylate. In the saponification of salol by sodium amyloxide, one product is amyl salicylate. The bearing of these facts on observations of Claisen (*Ber.*, **20**, 646) is pointed out. W. D. H.

Saponification of Tallow. By H. N. WARREN (*Chem. News*, **63**, 143).—Complete saponification is effected by boiling the fat, in a copper pan, with a solution of equal parts of sodium and potassium hydroxides for about 10 minutes. The fatty acids are liberated with dilute sulphuric acid, washed, dried by blowing air through the molten acids, and the solidifying point taken in the usual manner.

D. A. L.

Estimation of Grease. By W. L. GADD and S. LEES (*Chem. News*, **63**, 86).—In order to break the fall of the reflux ether and prevent its washing solid material into the flask below, when extracting light or finely pulverised matter in a Soxhlet apparatus, it is proposed to furnish the extraction tube with an annular projection inside (above the substance), upon which is placed an inverted glass cup, provided with a short stem to facilitate removal and with channels in its periphery, through which the reflux ether passes and flows quietly down the sides of the extraction tube, without disturbing the material in the filter. D. A. L.

The Analysis of Oleïn. By A. KÖRNER (*Chem. Centr.*, 1891, i, 218—219; from *Deut. Chem. Zeit.*, **5**, 402).—The separation of the unsaponifiable portion of oleïn is effected by the author as follows:—3—4 grams of oleïn is saponified with a slight excess of $\frac{1}{10}$ or $\frac{1}{2}$ N. alcoholic potash, mixed with a considerable quantity of ignited sand, evaporated to dryness, and the residue extracted in a 300—400 c.c. flask with 150 c.c. of hot ether, with addition of some alcohol.

To this solution is added an ethereal solution of mercuric chloride (2·42 parts of mercuric chloride to 1 part of potassium hydroxide employed) with addition of alcohol. The mercuric salts of the fatty acids separate as a voluminous precipitate, which is allowed to subside, the clear solution filtered off, the precipitate washed with ether, and the ether distilled from the filtrate until this measures about 30 c.c. This residual solution is brought to dryness in a porcelain dish, the residue extracted four or five times with 10 c.c. of light petroleum (boiling point below 50°), and the petroleum evaporated off again and the residue weighed. J. W. L.

General and Physical Chemistry.

Rotatory Dispersion of Tartrates. By G. KÜMMEL (*Ann. Phys. Chem.*, [2], **43**, 509—515).—The optical rotation of solutions of the normal tartrates of potassium, sodium, lithium, and ammonium, and of certain of their double salts, was determined for the Fraunhofer lines C, D, *b*, F, and G. The solutions taken were all of normal concentration, and the temperature of the observations was 15°. The dispersion was found to be the same for all the salts examined. Observations with solutions of different concentrations showed that the rotation is proportional to the concentration. Solutions of the acid tartrates of sodium and lithium were also examined, but in this case the concentration was only half that of the solutions used in the previous experiments. owing to the sparing solubility of these salts. The acid salts differ wholly in their behaviour from the normal salts, and the results are such as to justify the assumption that in aqueous solution these salts are decomposed into free acid and normal salt. On the above assumption, a calculation of the optical rotations of the solutions of the acid salts gave numbers in close agreement with those observed. H. C.

Sensitisers for Rays of Low Refrangibility. By G. HIGGS (*Proc. Roy. Soc.*, **49**, 345—346).—Directions are given for preparing solutions of the hydrogen sulphite compounds of alizarin-blue S and of cœrulin, to be used as sensitisers. The actinic curves for the two substances are almost identical. Whilst possessing, in a high degree, sensitising properties for rays throughout the region comprised between λ 6200 and 8000, they do not lower the sensitiveness to the violet and ultra-violet. Numerous lines in the spectrum have been depicted which previously were not known to exist. J. W.

Is Chemical Action affected by Magnetism? By M. LOEB (*Amer. Chem. J.*, **13**, 145—153).—The close relationship between electricity and chemical affinity on the one hand, and that between electricity and magnetism on the other, have naturally raised the question whether any relation can be traced between affinity and magnetism. All experiments hitherto made have failed to answer this question, as certain non-chemical phenomena have always been introduced, due either to the inequalities in the magnetic field or to the physical heterogeneity of the reacting system, or to both of these causes at once, whereas the conditions to be realised are that the system remains homogeneous throughout, and the field of stress also practically homogeneous. Such conditions can be realised by observing the speed of some reaction which does not involve solids, in the presence of a magnet, and again, when there is no magnetic effect, provided the magnetic properties of the system could be altered by the reaction. We might then expect that a reaction which made a system more or less amenable to magnetic action, might show evidence of acceleration or retardation by the magnetic force. Wiedemann has shown that in the ordinary form of reaction between salts, involving merely a double decomposition, the total magnetism of the system remains unaltered, but there is a marked change when the constitution of one of the ingredients is altered; the atomic magnetism of trivalent iron is 25 per cent. greater than that of the same element in the ferrous state. The author has, therefore, studied the effect of magnetism on the speed of oxidation and reduction of iron salts in solution by reagents which showed but a feeble magnetism by themselves. Two reactions were selected, namely, the oxidation of ferrous sulphate by potassium chlorate, and the reduction of ferric chloride by hydriodic acid. The results were negative and lead to the conclusion that no relation exists between magnetism and chemical affinity. H. C.

Method of Standardising Platinum Thermometers with reference to the Boiling Point of Sulphur. By H. L. CALLENDAR and E. H. GRIFFITHS (*Proc. Roy. Soc.*, **49**, 56—60).—Callendar (*Phil. Trans.*, 1887, A, 161) has shown that the difference between the readings of an air thermometer and a platinum resistance thermometer between 0° and 700° is closely represented by the formula $\delta\{(t/100)^2 - t/100\}$, δ being a constant for each particular wire. The present paper shows how to find δ by a single observation at a temperature other than 0° and 100°. The authors choose the boiling point of sulphur for this standard temperature; this was carefully ascertained by means of an air thermometer protected from radiation by two coaxial tubes, the inner one of metal, the outer of glass. The boiling point was found to be 444·53°, probably correct to a tenth of a degree. To obtain the constant, the boiling point with the platinum thermometer is found, and the difference between it and the above number equated to the expression containing δ.

A list of various corrected melting and boiling points obtained with different platinum thermometers is appended, the agreement being good. J. W.

Determination of the Boiling Point with Small Quantities of Material. By H. C. JONES (*Ber.*, **24**, 2251).—The author draws attention to the fact that some time ago (Trans., 1878, 175) he described a form of apparatus essentially identical with that recently described by Schleiermacher (this vol., p. 873) for determining the boiling point with small quantities of material. F. S. K.

Hydrogenation of Closed Chains. By F. STOHMANN and C. KLEBER (*J. pr. Chem.* [2], **43**, 538—544).—The authors have determined the following thermochemical data since their last communication (this vol., p. 376):—

	Heat of combustion. Cal.	Heat of formation. Cal.
$\Delta_{2.5}$-dihydroterephthalic acid ..	845·4	182·6
Dihydrophthalic acid	843·1	184·9
Δ_2-tetrahydrophthalic acid	881·6	215·4
Fumaroïd hexahydromellitic acid	923·9	618·1

The heat of combustion of mellitic acid is 788·2 Cal. (Abstr., 1889, 1096). It has been shown (this vol., p. 376) that the heat of combustion of a hexahydro-compound of a benzene-ring derivative is generally 68·7 + 2 × 45·3 Cal. higher than that of the benzene-ring compound, and by this rule the heat of combustion of hexahydromellitic acid should be 788·2 + 159·3 = 947·5 Cal., and not 923·9 Cal. From this it would appear that an excess of energy is stored up in mellitic acid so that less energy is brought into play in its conversion into the hexahydro-compound than is necessary in other cases.

A list is given to demonstrate the agreement between the hydrogenated compounds of the terephthalic series and those of the phthalic series.

The thermal value for the splitting up of the benzene-ring into an open chain has already been given as 54·8 Cal. for every 2 atoms of hydrogen added (*loc. cit.*); this is nearly true in the case of hexahydromellitic acid, for which the numbers vary from 51·5 to 55·0 for two atoms of hydrogen. A. G. B.

Determination of the Specific Gravity of Viscid Substances. By J. W. Brühl (*Ber.*, **24**, 2455—2457).—The author is of opinion that the apparatus described by Scheibler for the determination of the specific gravity of viscid substances (this vol., p. 520) is valueless for exact work with small quantities, since it is open to the same objections as the specific gravity bottle supplied with a capillary bored stopper. W. P. W.

Diffusion of Ammonia through Water and through Alcohol. By J. Müller (*Ann. Phys. Chem.* [2], **43**, 554—567).—The volume of ammonia absorbed by a given quantity of water in equal periods of time continually decreases until at length the amount becomes stationary. When this condition is reached, the amount of gas which diffuses through the liquid in a given time is directly proportional to the area, and inversely proportional to the length of the liquid column. The volume in cubic centimeters, which will diffuse through a column of 1 cm. length and 1 c.c. area in one minute under a pressure of 1 cm. of mercury, may be termed the diffusion constant. The change of this constant with the temperature is similar to that of the absorption coefficient of the gas by water, and the diffusion constant is therefore proportional to the absorption coefficient. Between 0° and 40° the diffusion constant seems to be proportional to the absolute temperature.

With ammonia and alcohol similar results to those given above were obtained. The proportionality between the diffusion constants and the absorption coefficients appears to be general. This is seen from the fact that at 20° the diffusion constants for water and alcohol are 0·093 and 0·047, and the absorption coefficients for the same temperature are 690 and 340. H. C.

Objections raised against the Hypothesis of Electrolytic Dissociation. By S. ARRHENIUS (*Ber.*, **24**, 2255—2264).—The author criticises the observations of Traube on the freezing points of dilute solutions of cane sugar (this vol., p. 874), and shows that his results are not in agreement with those of Raoult, Tammann, or Pickering. Traube gives a value for the molecular reduction in very dilute cane-sugar solutions of 36·8, but that which the author deduces from his own and Tammann's observations is only 19·5. This would contradict Traube's conclusion that non-electrolytes, such as cane-sugar, behave abnormally in very dilute solutions, and give values for the molecular reduction, which are similar to those obtained for non-electrolytes. The above conclusion is also contradicted by Pickering's observations on the behaviour of non-electrolytes in very dilute solutions, as the seven substances which he examined gave practically normal results for the molecular reduction. The author finds nothing in Pickering's recent results on the freezing points of mixed solutions which is opposed to the dissociation hypothesis. H. C.

Distribution of a Substance between Two Solvents, &c. By W. NERNST (*Zeit. physikal. Chem.*, **8**, 110—139).—This paper contains a theoretical and experimental investigation of the distribution of a substance between two solvents, which are either immiscible or only partially miscible, on the basis of the osmotic pressure and electrolytic dissociation theories. The case of the vapour pressure and boiling point of dilute solutions of volatile substances is also considered.

The agreement between calculated and observed values is satisfactory, and the author shows that valuable information regarding the molecular weights of substances in solution may be obtained in this way when other methods are inapplicable. J. W.

Relation between Affinity and Partition Coefficients in Immiscible Solvents. By P. AULICH (*Zeit. physikal. Chem.*, **8**, 105—109).—Substances which do not act chemically on each other are distributed each in a constant ratio between two solvents which are themselves immiscible. The author puts the question:—What happens if four substances which are in chemical equilibrium (for example, two acids and their salts with the same base) are distributed between two immiscible solvents? Here there are two sorts of forces which determine the final equilibrium, namely, chemical and physical. Various cases are discussed, and the author concludes that there must exist some ascertainable relations between the physical and chemical forces at work if the second principle of thermodynamics is to be upheld. J. W.

Affinity Coefficients of Bases. By E. LELLMANN and H. GROSS (*Annalen*, **263**, 286—299).—The authors have made a further series of determinations of the affinity coefficients of bases, employing the method previously described (this vol., p. 638). The values of κ in the case of α- and β-naphthylamine were found to be 0·03384 and 0·02593 respectively; in the case of metachloraniline $\kappa = 0·05112$, and in the case of tetrahydroquinoline $\kappa = 0·01333$. These values are the average result of concordant experiments made with solutions of different concentrations.

In all the experiments carried out up to this point, Guldberg and Waage's law has been found to hold good, but in the case of ortho- and para-amidobenzoic acid, metanitraniline, and thiohydantoïn, the value of κ in dilute solutions of the hydrochloride of the base varies greatly with the concentration, diminishing as the solution becomes more dilute; when, however, sufficiently concentrated solutions are employed, the value of κ remains constant. The behaviour of paramidobenzoic acid may be quoted as an example:—When a dilute solution, containing only 216·4 milligrams of the hydrochloride per litre, is employed, the value of κ is found to be 0·05965, but when the solution contains only 86·55 milligrams this value falls to 0·04284; when, on the other hand, a concentrated solution, containing 2769 milligrams of the hydrochloride, is used, the value of κ is 0·08495, and even on diluting the solution until it contains only 692·4 milligrams, the observed value remains 0·08947. The explanation of this phenomenon is probably to be sought for in some change in the configuration of the molecule brought about by an alteration in the degree of concentration of the solution.

Up to the present time the symbol κ has been used to denote the affinity of "butter-yellow" for hydrochloric acid, compared with that of a given base for this acid; in future κ will be employed to denote the reciprocal of this number, so that its value will increase, instead of decrease, as the affinity of the base increases. The affinity coefficient of aniline will be taken as unity, as it is one of the commonest organic bases, the hydrochloride of which is easily obtained in a pure condition; this coefficient, in accordance with the above statement, is the ratio between the number of molecules of hydrochloric acid in combination with the aniline and the number of molecules of hydrochloric acid in combination with the "butter-yellow," in a solution formed by dissolving equivalent quantities of the three substances under the conditions already described. F. S. K.

Velocity of Reaction between Metals and Halogens. By A. SCHÜKAREFF (*Zeit. physikal. Chem.*, **8**, 76—82).—Thin plates of the metal, 20 mm. by 40 mm., were rolled into a little cylinder, dipped into strong hydrochloric acid, and then washed with water. Thus prepared, they were dipped into a solution of the halogen, and left there for 15 minutes, the vessel being occasionally shaken. The halogens were dissolved in 1/50-normal solutions of the corresponding compounds with potassium. Before and after the experiment the solutions were titrated with thiosulphate solution, the diminution of the titre measuring the extent to which the reaction had taken place in the given time. A constant was calculated from Guldberg's formula, $k = \frac{lg C_0 - lg C_n}{T}$, where C_0 and C_n are the concentrations, and T the time in minutes. This formula was found to be not quite applicable, the constant usually changing somewhat with the initial concentration. The quantities of halogen reacting during a given time in equally strong solutions on equal surfaces of most (probably all) metals are equal; or, in other words, the quantities of metal reacting in a given time at equal or equivalent concentrations, are proportional to the atomic weight of the metal, and inversely proportional to its valency in the compound formed.

The metals examined were zinc, aluminium, iron, copper, and tin.

J. W.

Reaction between Ferric Salts and Soluble Thiocyanates. By G. MAGNANINI (*Zeit. physikal. Chem.*, **8**, 1—5).—Gladstone observed that the colour of an aqueous solution containing ferric chloride and potassium thiocyanate became more intense when excess of either of the salts was added. This points to the existence of a balanced action between the substance, and the author has made spectrophotometric observations with a view to settle the question. According to Guldberg and Waage's law, solutions should have the same coefficient of extinction when they contain in equal volumes p equivalents of the one salt and q equivalents of the other, no matter whether p refers to KCNS or to $FeCl_3$, provided that there is a balanced action. The author finds this to be the case, and also that the quantity of ferric thiocyanate formed is a regular function of the quantities of potassium thiocyanate and of ferric chloride dissolved in a given volume. He therefore assumes the action to be $FeCl_3 + 3KCNS \rightleftarrows Fe(CNS)_3 + 3KCl$.

Krüss and Moraht found that the maximum of extinction took place when the salts were present in the proportion of $FeCl_3$ to 12KCNS, and concluded that a stable double salt, $Fe(CNS)_3,9KCNS$, was formed in the solution. The author could not confirm this observation.

J. W.

The Dead-space in Chemical Reactions. By LIEBREICH (*Zeit. physikal. Chem.*, **8**, 83—104).—In a previous paper (Abstr., 1890, 1207), the author considered the shape of the dead-space formed in the reaction between chloral and sodium carbonate, and in that between iodic and sulphurous acids; and concluded that the physical character of the liquid immediately adjoining the containing walls and the free surface, was in such a degree different from that of the other parts of the liquid as to offer a certain degree of resistance to any chemical action taking place within it. He now proceeds to show, by means of various experiments, that there is a special resisting power near the surface of liquids. Cartesian divers were sunk to a considerable distance below the surface of a vessel containing water, &c. The additional pressure necessary to effect this being then suddenly removed, the diver rose, but could not penetrate the superficial layer, rebounding from it as from a solid wall.

Experiments were also made on the convection of liquids. Solutions of glycerol were employed, a light solution (coloured with azorubin) being allowed to ascend in a heavier. Vessels of various forms were employed, but it always appeared that the coloured liquid never reached the free surface, nor the walls in any capillary space unless there was subsequent diffusion.

The author replies to several criticisms on his views, and rejects the explanation given by Budde (this vol., p. 975) that the dead-space in the chloroform reaction is due to superficial evaporation and diffusion.

J. W.

Autocatalysis. By W. Ostwald (*Chem. Centr.*, 1891, i, 486; from *Abhdl. math.-phys. Klasse K. Sachs. Ges. Wiss.*, 1890, 189—192).—The conversion into lactones by elimination of water to which hydroxy acids are subject in aqueous solution in presence of another acid, occurs in the case of γ-hydroxyvaleric acid, when merely dissolved in water; this is explained by the author on the assumption that the acid is in part dissociated, and that the free hydrogen ions act catalytically. The presence of a salt of the acid, for instance the sodium salt, in the solution, retards the formation of the lactone very considerably, and the amount of free acid in the solution, as determined alkalimetrically, remains constant for days together. The author considers that this fact supports the above assumption, there being fewer free hydrogen ions present. J. W. L.

Isomorphism. By J. W. Retgers (*Zeit. physikal. Chem.*, **8**, 6—75).—The method adopted by the author for the detection of isomorphism in the experiments of which an account is here given, was the investigation of the colour of the crystals obtained when a coloured and a colourless salt were allowed to crystallise simultaneously from solution. Two salts, say potassium perchlorate and potassium permanganate, were dissolved in water, and a drop of each of the warm solutions brought on to a microscopic slide. The drops were either mixed, or connected by a narrow streak of liquid so that slow diffusion might take place.

If the salts, like those mentioned, are isomorphous, then crystals of all depths of colour are obtained; sometimes one crystal even may be of different depths at the two ends, with all intermediate shades between. If the two salts are not isomorphous (for example, potassium chloride and potassium permanganate), the crystals which separate show no transition, but are either colourless or dark-red (black). The thickness of the crystals is always very nearly the same, so that no disturbance is to be feared from this cause. If good results are to be obtained, the colour of one of the substances must be very intense; the blue copper salts can only be of service when the crystals formed are very thick.

By means of the above method, taken in conjunction with the usual crystallographic and optical examination of the salts, the author has studied the series $M'R^{vii}O_4$, using permanganates as the coloured salts, and $M_2'R^{vi}O_4$, the manganates being the standard crystals. He adopts as axiom: things that are isomorphous with the same thing are isomorphous with each other.

$KMnO_4$, $(NH_4)ClO_4$, $KClO_4$, $RbClO_4$, $CsClO_4$ are isomorphous. $LiClO_4,3H_2O$ and $LiMnO_4,3H_2O$ form mixed crystals; $NaClO_4,3H_2O$ and $NaMnO_4,3H_2O$ were too deliquescent for examination. $AgClO_4$ crystals were coloured by an unstable rhombic modification of $AgMnO_4$; the mixed crystals are strongly pleochroic, changing from blue-green to ruby-red with a rotating nicol. Periodates were not thoroughly examined. The author made several attempts to obtain perbromates, but failed.

Mixed crystals containing potassium manganate keep their blue-green colour for weeks. Ammonium salts cannot be investigated along with manganates, as they at once change the green colour to blood-red. When potassium salts are being studied, the addition of caustic potash produces very sharply-defined crystals.

K_2SO_4, $(NH_4)_2SO_4$, Rb_2SO_4, Cs_2SO_4, Tl_2SO_4, K_2SeO_4, Rb_2SeO_4, Cs_2SeO_4, Tl_2SeO_4, K_2CrO_4, Rb_2CrO_4, Cs_2CrO_4, K_2MnO_4, Rb_2MnO_4, Cs_2MnO_4 are all isomorphous, forming rhombic (pseudo-hexagonal) prisms and pyramids. $(NH_4)_2SeO_4$ forms monoclinic plates. $(NH_4)_2CrO_4$ and Tl_2CrO_4 are very slightly soluble; the former has probably an isodimorphous relationship with K_2CrO_4. Na_2SO_4, Ag_2SO_4, Na_2SeO_4, Ag_2SeO_4 are isomorphous,—rhombic pyramids, strongly birefringent. Ag_2CrO_4, Na_2CrO_4, and Na_2MnO_4 are probably isomorphous. So are the anhydrous sulphate, chromate, and selenate of lithium; the manganate does not exist. Manganese dioxide is not attacked by fused lithium carbonate.

The double salts in the above groups were also studied to some extent. $KLiSO_4$ and $KLiSeO_4$ are not isomorphous, but morphotropic.

The author succeeded in showing that K_2WO_4 and K_2MoO_4 are isomorphous with K_2MnO_4. Between sulphates and selenates there is mostly direct isomorphism; between sulphates and chromates isodimorphism often occurs, and between sulphates and molybdates or tungstates it is the rule. K_2UO_4 could not be prepared.

The author failed to prepare an anhydrous salt, K_2TeO_4 isomorphous with K_2SO_4, &c. The only examples of isomorphism between tellurium and sulphur being in the tellurides and sulphides of silver and lead, he is inclined to assert that the two elements are not isomorphous, and would suggest placing tellurium (at. wt. = 128) in the eighth periodic group along with ruthenium and osmium, to which it exhibits certain analogies. J. W.

Vacuum Desiccator arranged for Evaporation at any desired Temperature. By J. W. Brühl (*Ber.*, **24**, 2457—2459).—Feeling the want of an apparatus in which a dissolved substance, especially one prone to decompose in solution and at higher temperatures, can be rapidly freed from the solvent and crystallised, the author has devised a vacuum desiccator in which evaporation can be carried on at any desired temperature. The plate of an air-pump is provided with two holes in addition to the one through which the bell-jar is exhausted. Through these holes pass two brass tubes about 12 cm. long and 1 cm. in diameter, which stand about 7—8 cm. above the plate, and are fixed airtight by means of caoutchouc washers and brass nuts.

The tubes are soldered above the plate to a circular box about 15 cm. in diameter and 1 cm. high, made of copper plate 2 mm. thick, and provided with internal supports to prevent bulging when the bell-jar is exhausted. The circular box serves to support the vessel containing the solution to be evaporated, and is heated by steam, hot air, or other vapours led through the brass tubes. W. P. W.

Inorganic Chemistry.

Slow Combustion of Gaseous Mixtures. By A. KRAUSE and V. MEYER (*Annalen*, **264**, 85—116).—When moist electrolytic gas is heated at 305° in glass vessels over mercury for 1—2 weeks, combination takes place between the oxygen and hydrogen, and only a very small volume of gas remains; in absence of mercury, combination takes place only very slowly at 305°, and at 448° the diminution of volume is very small, but at 518° a considerable quantity of water is produced. The thin glass bulbs provided with lateral capillary tubes, which were employed in most of these experiments, can be sealed without danger of explosion if a little air is permitted to enter the point of the capillary, but even traces of air or other impurities have such a great influence on the reaction that the results are very variable, and, consequently, the relation between the time and the amount of combination could not be determined.

The temperature of explosion of electrolytic gas, and that of a mixture of oxygen and carbonic oxide in theoretical quantities, lies between 518° and 606° when thin, sealed glass vessels are employed.

A number of experiments were made in order to try and determine the rate of combination of oxygen and hydrogen under certain conditions. For this purpose, electrolytic gas, generated by the electrolysis of hot water, and consequently free from ozone and hydrogen peroxide, was passed for many days through a series of bulbs, fused together by means of very small capillary tubes. The apparatus was very carefully cleaned, the gas was dried with concentrated sulphuric acid, and indiarubber, cork, and all organic substances were carefully excluded; in some of the experiments, the bulbs were heated at a faintly, dull-red heat, and the pure electrolytic gas passed for eight days. The bulbs were then sealed before the blowpipe, and heated in the vapour of sulphur or of phosphorus pentasulphide (b. p. 518°) under the same conditions. In spite of all precautions, the results of the experiments were very variable, and no relation between time and amount of combination could be determined; it would seem, therefore, that the glass surface, even when most carefully cleaned, has a modifying but variable action on the electrolytic gas, and that this action is sufficiently different, even in the case of two exactly similar bulbs, to cause great irregularities in the experiments.

Bulbs containing pure dry, or moist, electrolytic gas can be sealed without danger when the capillary tube is sufficiently fine ($\frac{1}{4}$ to $\frac{1}{3}$ mm. in internal and 4 mm. in external diameter); in the case of the moist gas, a small flame can be observed running along the capillary, when the tube is being sealed, but it goes out before reaching the bulb; no flame is seen in the case of the dry gas, the volume of which undergoes no appreciable diminution by combination taking place.

The electrolytic gas employed in the above experiments was found on careful examination to be free from any appreciable quantity of air.
F. S. K.

Atomic Weight of Oxygen. By E. H. KEISER (*Amer. Chem. J.*, **13**, 253—256).—The method described involves the complete synthesis of water, that is, the determination of the weight of water resulting from the combination of known weights of hydrogen and oxygen. Pure hydrogen is passed into a weighed exhausted vessel containing spongy palladium, the increase in weight after a second exhaustion giving the amount occluded. An excess of pure oxygen is then admitted, and combination takes place at the ordinary temperature under the influence of the palladium. The whole amount of oxygen having been determined by a third weighing, the excess, together with the synthetised water, is exhausted from the vessel, the water being collected in a phosphorus pentoxide tube; the decrease in weight of the vessel and tube corresponds to the oxygen removed, whilst the increase in that of the tube gives the amount of water formed. Trial determinations have given good results.

The author replies to the criticism of Noyes (*J. Anal. Chem.*, **5**, 36; *Ber.*, **24**, 238).
JN. W.

Atomic Weight of Oxygen. By W. A. NOYES (*Amer. Chem. J.*, **13**, 354—355; compare Abstr., 1890, 1370; 1891, 523).—A rejoinder to the remarks of Keiser (preceding abstract).
JN. W.

Reaction between Hydrogen Arsenide and Silver Nitrate. By L. MARCHLEWSKI (*Ber.*, **24**, 2269—2271).—The products of the action of hydrogen arsenide on a solution of silver nitrate, according to Laissaique (*Journ. Chem. Med.*, **16**, 685), are free nitric acid, silver, and arsenious anhydride. In order to test the truth of this statement the author has determined the strength of nitric acid necessary to dissolve finely-divided silver. The nitric acid was freed from nitrous acid by a current of carbon dioxide. The finely-divided silver was then treated in the cold with the pure acid; the mixture filtered and the filtrate tested for silver nitrate and nitrite. The results show that 0·4 per cent. of nitric acid is sufficient to attack the silver, and that with a solution containing 0·7 per cent. a considerable quantity is dissolved. The author also shows that pure dilute nitric acid, when treated with decinormal arsenious acid, is converted into nitrous acid, and that nitric acid containing a trace of nitrous acid dissolves silver much more readily than the pure acid.

The above results show that the action of hydrogen arsenide on a solution of silver nitrate cannot take place as stated by Laissaique, for the precipitated silver would be redissolved by the nitric and nitrous acids formed at the same time. E. C. R.

Action of Light on Silver Chloride. By R. HITCHCOCK (*Amer. Chem. J.*, **13**, 273—277).—A continuation of previous work (Abstr., 1890, 213). Slips of microscopic cover glass coated with a thin layer of the chloride were exposed to direct sunlight for about four months, and weighed from time to time. The loss of chlorine was greater than in the former experiments, and varied from 0·0821 to 0·0929 gram per gram of silver chloride. Probably even then the decomposition was not complete. On digestion with dilute nitric acid, the product gave up a quantity of silver equivalent to the amount of chlorine liberated; hence it would seem that the action of light merely separates the chlorine from the silver. JN. W.

Preparation of Crystalline Barium and Calcium Fluorides. By H. MOISSAN (*Bull. Soc. Chim.* [3], **5**, 152).—Calcium chloride solution (10 per cent.) is added to a boiling solution of potassium fluoride (0·5 per cent.) in a platinum capsule, and the mixture is boiled for 30 minutes; the collected precipitate is washed, dried, and calcined; the microscopic crystals thus obtained are transparent and correspond with the formula CaF_2. Microscopic crystals of barium fluoride are obtained when solutions of barium chloride (3 6 per cent.) and potassium fluoride (1 per cent.) are similarly treated.

T. G. N.

Reduction of Oxides by Magnesium. By C. WINKLER (*Ber.*, **24**, 1966—1984).—In his last communication the author was inclined to regard lanthanum as a member of the fourth group in the periodic system, since it forms a hydride and thus resembles the majority of the elements in that group (this vol., p. 802), but this view is now abandoned in consequence of Brauner's determination of the atomic weight of the element (this vol., p. 881). The present paper deals with the preparation of hydrides of elements in the second and third groups of the periodic system by reduction of their oxides by magnesium in an atmosphere of hydrogen. The method is inapplicable in the case of lithium, sodium, potassium, and rubidium hydroxides or carbonates, since any hydrides formed would be decomposed at the temperature of the reaction—the known hydrides of sodium and potassium being dissociated at moderately high temperatures. Reduction of cæsium hydroxide and carbonate gave no evidence of the formation of a hydride.

Beryllium.—When beryllium oxide (1 mol. prop.) was heated with magnesium (1 at. prop.) in a current of hydrogen for four hours at a red heat, a slow absorption of the gas took place, and the product on analysis had the composition:—

BeH.	BeO.	MgO.	Mg.	Total.
3·33	45·40	45·03	6·24	100·00

indicating that not more than 14 96 per cent. of the beryllium employed had been converted into hydride. The product had an unpleasant odour, and on treatment with warm water gave off hydrogen slowly. When heated in a current of oxygen, a distinct hydrogen flame and the formation of water were observed.

Magnesium.—When magnesium oxide was reduced under the conditions just described, a slow absorption of hydrogen took place with the formation of a product of the composition:—

MgH.	MgO.	Mg.	Total.
3·54	82·06	14·40	100·00

indicating that not more than 6·42 per cent. of the magnesium had been converted into hydride. The product had an unpleasant odour, evolved hydrogen slowly on treatment with water, and when heated in a current of oxygen gave evidence of the formation of water.

Calcium.—In the case of lime, the absorption of hydrogen was much more rapid and was complete at the end of four hours. The product had the composition:—

CaH.	CaO.	MgO.	Mg.	Total.
33·14	28·31	37·66	0·89	100·00

showing that 61·52 per cent. of the calcium employed had been converted into hydride. On exposure to the air it swelled up and fell to powder, and on treatment with water evolved hydrogen very rapidly. When heated, it burned with a slightly luminous flame in air, and with slight explosion in oxygen producing water in noteworthy quantities.

Strontium.—On reduction under the above conditions, strontium oxide rapidly absorbed hydrogen during two hours with the formation of a product of the composition:—

SrH.	SrO.	MgO.	Mg.	Total.
66·23	4·17	28·93	0·77	100·00

indicating that 94·91 per cent. of the strontium employed had been converted into hydride. On exposure to the air it was readily oxidised, hydrogen being evolved and strontium hydroxide formed, and on treatment with water hydrogen was rapidly given off. It burned either in air or oxygen with a hydrogen flame, a slight explosion attending the combustion in oxygen.

Barium.—The baryta employed had the composition:—

BaO.	$Ba(OH)_2$.	$BaCO_3$.	Al_2O_3.	SiO_2.	Total.
71·26	18·13	7·34	1·87	1·40	100·00

and on reduction under the above conditions absorbed hydrogen very rapidly during two hours, with the formation of a product which gave the following numbers on analysis:—

BaH.	BaO.	MgO.	Al_2O_3.	SiO_2.	O_2(excess).	Total.
70·33	4·27	20·99	1·66	0·97	1·73	100·00

corresponding with the conversion of 94·66 per cent. of the barium into hydride. In properties the compound closely resembled the strontium hydride.

The author concludes this portion of his paper with speculations as to the composition of the atmosphere of the sun and fixed stars.

In the third group, boric anhydride and alumina were submitted to reduction in hydrogen with negative results, but yttrium was found to resemble lanthanum in forming a hydride, although the conversion was not so complete. When yttrium oxide was reduced under the conditions already given, absorption of hydrogen took place rapidly and was complete at the end of an hour. The product had the composition :—

Y_2H_3.	Y_2O_3.	MgO.	Mg.	Total.
12·88	72·56	10·15	4·41	100·00

indicating that 18·44 per cent. of the yttrium employed had been converted into hydride. On treatment with boiling water, it gave off a very small quantity of hydrogen, and when heated in oxygen it burned with a feebly luminous flame. W. P. W.

Action of Ammonia on Zinc Chloride. By W. KWASNIK (*Arch. Pharm.*, **229**, 310—316).—The action of ammonia on zinc chloride has frequently been studied, but always in the presence of water. An alcoholic solution of zinc chloride treated with an alcoholic solution of ammonia, or with gaseous ammonia, until the odour of ammonia just begins to persist, yields a precipitate which does not dissolve on further addition of ammonia. The product is a light, pure white, odourless, crystalline powder, $ZnCl_2,2NH_3$. The powder is insoluble in water and alcohol, easily soluble in dilute acids, aqueous ammonia, soda, and potash ; in the two latter with evolution of ammonia. Heat is developed on dissolving it in acid. The compound is stable in the air. By distillation in a hard-glass retort a transparent, glass-like, hygroscopic compound, $ZnCl_2,NH_3$, was obtained. J. T.

Basic Zinc Sulphite. By K. SEUBERT (*Arch. Pharm.*, **229**, 316—328).—On mixing equal volumes of boiling normal solutions of zinc sulphate and sodium sulphite (28·7 grams $ZnSO_4 + 7H_2O$ and 31·5 grams of 40 per cent. sodium sulphite each dissolved in 100 c.c.), a precipitate of basic zinc sulphite, $8ZnSO_3,7Zn(OH)_2 + 7H_2O$, appears almost immediately. Decinormal solutions mixed at a moderate temperature, dilute zinc sulphite solution heated alone, or concentrated zinc sulphite solution largely diluted with water, yields a very voluminous precipitate of the basic zinc sulphite, $5ZnSO_3,8Zn(OH)_2$. The same basic salt is produced by boiling the normal or the monobasic sulphite for some time in water. J. T.

Nitrite of Potassium, Lead, and Copper. By VAN LESSEN (*Rec. Trav. Chim.*, **10**, 13—14).—On adding a mixture of copper nitrite and lead acetate solution to a large quantity of solution of potassium nitrite, and then adding acetic acid, a crystalline precipitate is obtained, which under the microscope is seen to consist of black, cubic crystals. When washed with alcohol and air-dried, the crystals are of a shining dark-green, they give a brown streak, and have a sp. gr of 3·345 at 15°. The aqueous solution is yellowish-green, and yields, by free evaporation in air, thin, yellowish-brown, hexagonal plates, which change again into the blackish cubical crystals described, on the addition of a concentrated aqueous solution of potassium nitrite and a little acetic acid.

The salt is anhydrous, may be dried without decomposition at 110—120°, and has the formula $PbCuK_2(NO_2)_6$. Hence the salt is much simpler than the corresponding cobalt compound analysed by Stromeyer. W. T.

Ternary Alloys. Part III. By C. R. A. Wright and C. Thompson (*Proc. Roy. Soc.*, **49**, 156—173; compare Abstr., 1890, 336; and this vol., p. 267).—When approximately equal weights of bismuth and zinc were melted together, and then poured, after stirring up, into red-hot, narrow, clay test-tubes, in which they were heated for over eight hours, the mixture separated into two layers, a solution of bismuth in zinc and a solution of zinc in bismuth. At 650° (approximately) the solutions contained 14·28 and 97·68 per cent. of zinc respectively; at 750°, 15·18 and 97·53 per cent.

When tin was added to the mixture in varying proportions, the extent of mixing of the bismuth and zinc was increased, the tin distributing itself between the two layers. Tables and curves are given to illustrate the composition of the mixtures obtained with varying proportions of tin and at different temperatures. Notable differences appear when the curves are compared with those previously obtained with zinc, lead, and tin. The solubility of zinc in bismuth is always greater than in lead, whether tin be absent, or present to a given extent, in each case.

Similar experiments were conducted with bismuth, zinc, and silver. The mixtures show the same behaviour as analogous mixtures of lead, zinc, and silver, leading to the conclusion that two definite compounds of zinc and silver are formed under appropriate conditions. These compounds correspond with the formulæ $AgZn_5$ and Ag_4Zn_5. The first mixes more freely with lead (or bismuth) than either pure zinc or the second compound, but is somewhat unstable on prolonged heating. The compound Ag_4Zn_5 is characterised by the peculiar red colour which is assumed by a recently cut surface on exposure to the air, and by being less soluble in lead (or bismuth), relatively to the zinc present, than either pure zinc or a mixture of zinc and silver in any other proportion. J. W.

Ternary Alloys. Part IV. Method of Graphic Representation. By C. R. A. Wright, C. Thompson, and J. T. Leon (*Proc. Roy. Soc.*, **49**, 174—193).—At the suggestion of Sir G. G. Stokes the authors have adopted a triangular mode of graphic representation analogous to that used by Maxwell for the composition of colours.

Stokes also drew their attention to the circumstance that the equilibrium between the two conjugate mixtures (see preceding abstract) should only depend on their composition at any given temperature, and not on their quantity. This conclusion was not in accordance with results previously obtained with alloys. To test it, the authors instituted experiments with mixtures of chloroform, water, and acetic acid, and found it verified (compare Duclaux, *Ann. Chim. Phys.* [5], **7**, 264, and Nernst, this vol., p. 1148). The probable reason that it is not exactly true for alloys, is that there is in this case incomplete intermixture, and also incomplete separation. J. W.

Decomposition of Potassium Manganate by Ammonium Salts. By J. W. Retgers (*Rec. Trav. Chim.*, **10**, 1—3).—The green colour of a solution of potassium manganate is changed by any acid to the red colour of the permanganate, the reaction proceeding according to the equation, $3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O$. The same change takes place in presence of water only if the latter be in large excess, $3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KOH + MnO_2$. A solution of manganate, to which has been added a solution of ammonium sulphate, containing a large quantity of free ammonia, undergoes the same change, in fact, if a small crystal of ammonium sulphate be plunged into an ammoniacal solution of potassium manganate, it rapidly becomes surrounded by a clear red zone, just as if a drop of acid had been introduced into the green solution. Any other salt of ammonium produces the same effect, but other neutral salts, such as sodium sulphate, do not excite any change. The decomposition by ammonium salts may be represented by the equation, $3K_2MnO_4 + 4NH_4Cl = 2KMnO_4 + MnO_2 + 4KCl + 4NH_3 + 2H_2O$. As solutions of potassium manganate are only stable in presence of a certain excess of potash or soda, the reaction is probably due to the acid in the ammonium salt, combining with the base of the manganate, giving ammonia and manganic acid, which appears not to form any ammonium salt, and hence at once decomposes; the decomposition seems to be quite analogous to that caused by ammonium salts with silicates of potassium or sodium. It is impossible to obtain isomorphous mixed crystals of ammonium sulphate and potassium manganate, whereas with potassium sulphate in various proportions they are readily formed. W. T.

Complex Inorganic Acids: Phosphotungstic Acids. By F. Kehrmann and M. Freinkel (*Ber.*, **24**, 2326—2335).—*Phosphododecatungstic acid*, $24WO_3,P_2O_5,3H_2O + xH_2O$, is prepared by mixing a hot saturated solution of sodium tungstate with sodium phosphate or phosphoric acid in the proportion of 12 mols. of tungstate to at least 1 mol. of phosphoric acid. To the mixture which becomes strongly alkaline hydrochloric acid is gradually added. Hydrated tungstic acid is precipitated, but again dissolves, and hydrochloric acid is then added until the normal sodium salt of the complex acid begins to separate. On cooling, the salt crystallises out, and is purified by recrystallisation from water, in which it is easily soluble. The *sodium* salt crystallises from a hot, saturated aqueous solution in large, transparent, colourless octahedra, which become opaque on exposure to air, and if allowed to remain in the solution, redissolve, and then separate in rhombohedral tablets, which are stable in air. The dry salt has the composition $24WO_3,P_2O_5,3Na_2O$. The *barium* salt is obtained in regular octahedra on adding a saturated solution of barium chloride to a solution of the sodium salt. It is somewhat less soluble than the sodium salt, and becomes opaque on exposure to the air. The dry salt has the composition $24WO_3,P_2O_5,3BaO$. Both these salts are colourless when pure. The *free acid* is obtained by precipitating a concentrated solution of the barium salt with dilute sulphuric acid, and on evaporating the filtrate, separates in large cubic crystals, which are easily soluble in water, and are stable to air. The acid is completely converted into the barium salt on adding a concentrated solution of barium chloride. On the addition of silver nitrate, the *silver* salt is obtained as a sparingly soluble, white powder. When potassium or ammonium salts are added to a solution of the acid or its salts in presence of mineral acids, a white powdery precipitate of the normal *potassium* or *ammonium* salt is formed; this is almost insoluble in water. The above acid completely corresponds to the analogous molybdenum compound, $24MoO_3,P_2O_5.3H_2O$, but is decomposed by alkalis in a different way.

The above insoluble potassium and ammonium salts dissolve easily in aqueous alkalis, and in alkaline carbonates with evolution of carbonic anhydride, yielding salts of an acid of the composition $22WO_3,P_2O_5,7H_2O$. The *barium* salt, $22WO_3,P_2O_5,7BaO + 53H_2O$, is most easily obtained by gradually adding powdered barium carbonate to a boiling concentrated solution of the salt $24WO_3,P_2O_5,3BaO$ as long as effervescence takes place. On cooling, it crystallises in lustrous octahedra, and is purified by recrystallisation from water containing a few drops of acetic acid. The *potassium* salt, obtained in a similar way to the barium salt, crystallises in large, colourless quadratic octahedra, and is easily soluble in water. The *ammonium* salt is very soluble. The solutions of these salts are neutral to litmus. The free acid could not be obtained. When a concentrated aqueous solution of the salt $22WO_3,P_2O_5,7K_2O$ is decomposed by hydrochloric acid, a precipitate of the salt $24WO_3,P_2O_5,3K_2O$ is obtained, and the mother liquors on the addition of potassium chloride deposit a salt, which crystallises in six-sided scales, and is very soluble in water. The barium salt, $22WO_3,P_2O_5,7BaO$, is decomposed in the same way.

The authors reserve the further discussion of this interesting reaction for a future communication. E. C. R.

Hydrate of Potassium Stannichloride. By J. MOREL (*Chem. Centr.*, 1891, i, 492; from *Bull. Soc. franc. Min.*, **13**, 339—341).—If a solution of potassium stannichloride be allowed to crystallise at a temperature below 25°, a new hydrate is obtained which crystallises in the prismatic system, and not in the regular octahedra as the salt is usually obtained. The faces observed are 110, 101, 010; axial ratio: $a : b : c = 0{\cdot}6843 : 1 : 0{\cdot}7588$. The analysis gave figures agreeing moderately well with the formula $K_2SnCl_6 + H_2O$.

J. W. L.

Sublimation of Antimony Trichloride. By C. HENSGEN (*Rec. Trav. Chim.*, **9**, 303—304).—A quantity of antimony trichloride is placed in a distillation flask provided with a side tube, and of about

1½ to 2 litres capacity; the flask is placed on a water-bath with the neck inclined downwards, and fitted by means of a good cork into a smaller flask serving as a receiver; the side tube passes vertically upwards, and is then bent and fitted with a drying tube. The water-bath is of such a size that the part of the flask containing liquid antimony trichloride is completely immersed in water-vapour when the sublimation is going on. The upper part of the flask is cooled by cold water dropped on to a piece of filter paper. When a sufficient quantity of the long, lanceolate crystals of the sublimate has collected on the cooled portion of the flask, the whole is allowed to cool slowly; and as soon as the trichloride on the bottom of the flask has solidified, the sublimate is shaken carefully into the receiver. The operation is then repeated until the whole of the charge has been sublimed. In this way 200 grams of sublimed trichloride can be readily prepared in a day. W. T.

Metallurgy of Bismuth. By E. MATTHEY (*Proc. Roy. Soc.*, **49**, 78—79).—The small proportion of copper frequently contained in commercial bismuth has hitherto been eliminated by a tedious wet process. The author finds that the copper may be completely removed by fusing the bismuth with successive small quantities of sodium monosulphide, and skimming off the scoria, which contains all the copper. 105 kilos. of commercial bismuth yielded 94 kilos. of bismuth free from copper, and 11 kilos. of skimmings. The temperature required is comparatively low, so that little loss by volatilisation is sustained. J. W.

Bismuth Bromide. By V. MEYER (*Annalen*, **264**, 122—125).—Bismuth bromide boils at 453°, as the average of three experiments made with the air thermometer devised by the author and Goldschmidt: the boiling point of bismuth chloride determined with a mercury thermometer was found to be 435—441° (uncorr.).
F. S. K.

Certain Properties of Metals considered in Relation to the Periodic Law. By W. C. ROBERTS-AUSTEN (*Proc. Roy. Soc.*, **49**, 347—356).—In a previous paper (*Phil. Trans.*, 1888, A, 339), the effect of about 0·2 per cent. of impurities on the mechanical properties of gold was examined, the results showing that metals which diminish its tenacity and extensibility have high atomic volumes, while those which increase these properties have either the same atomic volume as gold or a lower one. The behaviour of aluminium was exceptional. In the present paper, the mode of cooling of pure molten gold and of gold containing aluminium is studied. A thermoelectric couple of platinum and platinum containing 10 per cent. of rhodium was used, in conjunction with a mirror galvanometer and a photographic recording apparatus, to give a curve for the rate of cooling. Pure gold solidifies sharply at 1045°; the curve for gold containing lead is somewhat similar, but that for gold containing 0·47 per cent. of aluminium scarcely shows a distinct freezing point. The atomic depression of the freezing point for aluminium seems to be abnormally small. Silver present in gold, up to as much as 4 per cent., does not lower the freezing point. Aluminium combines with molten gold with great evolution of heat. J. W.

Colloïdal Sulphides of Gold. By E. A. Schneider (*Ber.*, **24**, 2241—2247).—Colloïdal aurous sulphide, Au_2S, can be prepared by saturating a solution of aurous cyanide in potassium cyanide with hydrogen sulphide, warming carefully with hydrochloric acid until a brown turbidity is produced, and then submitting the whole to dialysis; there remains in the dialyser a deep-brown, colloïdal solution of aurous sulphide which can be separated from the undissolved portions by decantation and filtration. The most concentrated solutions that can be obtained in this way contain 1·74 grams of the sulphide per litre. When the colloïdal solution is heated at 200—230°, sulphuric acid is formed, and gold is deposited; when the solution is frozen and melted again, the aurous sulphide is precipitated. On adding a colloïdal solution of ferric hydrate to the colloïdal solution of aurous sulphide, no reaction takes place even on warming.

Colloïdal auroauric sulphide, Au_2S_2, can be easily prepared by boiling the freshly precipitated sulphide with potassium cyanide until about one half of the sulphide is dissolved, and then submitting the remainder to dialysis; the dark-brown liquid obtained in this way is separated from the undissolved sulphide by decantation and filtration. The most concentrated solutions that can be obtained contain 0·8 gram of the sulphide per litre; when the solution is frozen, it behaves like the solution of aurous sulphide, but it undergoes no change when heated at 240°.

When auroauric sulphide, either the colloïdal or the ordinary modification, is warmed with a solution of auric chloride, the whole of the gold is deposited, with formation of hydrochloric acid and sulphuric acid; it is probable that the metallic gold found in nature has been formed in a similar manner by the action of hydrogen sulphide on solutions of auric chloride. F. S. K.

Derivatives of Carbonyl Chloroplatinite. By F. Mylius and F. Foerster (*Ber.*, **24**, 2424—2443).—Carbonyl chloroplatinite (Schützenberger, *Ann. Chim. Phys.* [4], **21**, 350; Pullinger, Trans., 1891, 598) has a distinctly basic character, and dissolves in excess of hydrochloric acid with a lemon-yellow colour, due to the formation of a very soluble and unstable substance, having probably the composition $COPtCl_2,HCl$. The solution of this hydrochloride is readily prepared by stirring the sublimate obtained in Schützenberger's reaction (*loc. cit.*) with concentrated hydrochloric acid for some time, since the dicarbonyl chloroplatinite which is also present is decomposed by the acid into carbonyl chloroplatinite, with the evolution of carbonic oxide containing a small proportion of carbonic anhydride. When rapidly evaporated to dryness in a vacuum, the solution leaves a crystallised residue of carbonyl chloroplatinite; on a water-bath, however, complete decomposition ensues, with the separation of metallic platinum. So long as the acid is concentrated, the solution of the chloroplatinite is stable; on dilution with water, no alteration seems to be produced for a short time, but suddenly the colour changes to brownish-black, and platinum separates in flocks, owing to an almost complete decomposition of the chloroplatinite into platinum, carbonic anhydride, and hydrochloric acid, as represented in Schützenberger's equation $COPtCl_2 + H_2O = CO_2 + Pt + 2HCl$, a very small portion only of the substance remaining unaltered in the acid solution. Concentration and temperature also have a marked influence on the stability of the solution, rise of temperature bringing about a similar decomposition. The separated platinum contains a trace of chlorine, but in contact actions and other respects resembles platinum black (cf., however, Pullinger, *loc. cit.*). The hydrochloric acid solution of the chloroplatinite is a powerful reducing agent, reducing silver, gold, and mercury salts from their solutions. On the addition of stannous chloride, the solution becomes yellowish-red, and on treatment with concentrated sulphuric acid and a trace of furfuraldehyde gives a purplish-red coloration.

Carbonyl chloroplatinite not only combines with hydrogen chloride, but also forms a series of yellow, crystalline, double salts with soluble metallic chlorides; these, however, are difficult of isolation, on account of their great solubility, and the readiness with which they are decomposed by water. Double salts of the general formula $COPtCl_2,RHCl$ are obtained by combination with the hydrochlorides of amines, and these, when not too soluble, serve as an additional means of characterising the bases.

Amylamine carbonyl chloroplatinite hydrochloride,

$$COPtCl_2,C_5H_{13}NHCl,$$

crystallises from dilute hydrochloric acid in golden-yellow scales, melts at 184°, and dissolves readily in alcohol and ethyl acetate, less readily in ether, benzene, and chloroform, but is decomposed by water, with the production of a black colour.

Aniline carbonyl chloroplatinite hydrochloride, $COPtCl_2,C_6H_7NHCl$, crystallises in lustrous, golden scales, melts, when rapidly heated, at 210—212° with decomposition and blackening, and is sparingly soluble in the ordinary solvents, with the exception of alcohol and ethyl acetate.

Pyridine carbonyl chloroplatinite hydrochloride, $COPtCl_2,C_5H_5NHCl$, forms strongly lustrous, transparent, golden-yellow prisms, and can be crystallised from dilute hydrochloric acid, but is slowly decomposed by water.

Quinoline carbonyl chloroplatinite hydrochloride, $COPtCl_2,C_9H_7NHCl$, crystallises from hydrochloric acid in bright-yellow needles, melts at 166°, and dissolves readily in alcohol and ethyl acetate. These compounds, when heated frequently, give a sublimate containing platinum, and it is possible that the loss of platinum so often noticed in analyses of platinochlorides is to be referred to the formation of compounds of this character, since it is conceivable that reactions may ensue between platinum, carbonic oxide, and chlorine during the combustion.

The determination of the percentage of carbonic oxide in these compounds by elementary analysis presents no difficulties, but as they evolve the gas on treatment with potassium cyanide, it is also possible to estimate the percentage volumetrically. The chief reaction is represented by the equation $COPtCl_2 + KCN = K_2Pt(CN)_4 + 2KCl + CO$, but the gas contains in addition from 3—8 per cent. of hydrogen, and a small proportion of carbonic anhydride. These in all probability owe their presence to two subsidiary reactions, one between the chloroplatinite and the alkaline solution of the cyanide with the production of carbonic anhydride and platinum, and a second between the platinum so obtained and the cyanide with the formation of hydrogen, in accordance with the equation $Pt + 4KCN + 2H_2O = K_2Pt(CN)_4 + 2KHO + H_2$, whence it follows that the amount of carbonic oxide in the compound is given by the sum of the volumes of carbonic oxide and hydrogen evolved. The analysis is conducted in an atmosphere of carbonic anhydride, and the liberated gas collected in an azotometer filled with caustic potash solution.

Carbonyl bromoplatinite (see Pullinger, *loc. cit.*) is formed when the hydrochloric acid solution of the chloroplatinite is evaporated on a water-bath in a current of hydrogen bromide, and can be freed from traces of platinum and platinous bromide by crystallisation from benzene. It crystallises in orange-red needles, melts at 181—182° without appreciable decomposition, and dissolves readily in benzene and hydrobromic acid, but is immediately decomposed by water into platinum, carbonic anhydride, and hydrogen bromide. It yields a series of crystalline double salts with metallic bromides and with the hydrobromides of amines, and of these *pyridine carbonyl bromoplatinite hydrobromide*, $COPtBr_2,C_5H_5N,HBr$, crystallises from hydrobromic acid in yellow needles, which melt at 203—205° without decomposition.

Carbonyl iodoplatinite, $COPtI_2$, is obtained by adding dilute hydriodic acid to the hydrochloric acid solution of carbonyl chloroplatinite, dissolving the resulting brick-red, amorphous precipitate in hydriodic acid, evaporating to dryness on a water-bath, and crystallising the residue from benzene. It is simpler, however, to evaporate the mixture of chloroplatinites obtained in Schützenberger's reaction with concentrated hydriodic acid, and purify the residue from platinum and platinous iodide by crystallisation from benzene. It forms red, rod-like crystals, which exhibit a violet shimmer, and resemble chromic anhydride in colour. It melts at 140—150°, decomposes with the liberation of iodine at a slightly higher temperature, and dissolves readily in benzene and ether. The alcoholic solution becomes turbid on warming, owing to the separation of platinous iodide, and later of platinum. Water decomposes it somewhat slowly, with the formation of a dark-coloured precipitate containing iodine; alkalis set platinum free, and potassium cyanide reacts with it, liberating carbonic oxide. Carbonyl iodoplatinite forms double salts with metallic iodides, and of these the compound with potassium iodide, $COPtI_2,KI$, crystallises in yellowish-brown scales, melts at 150—180° with decomposition, and is readily soluble in water, alcohol, and ether, but insoluble in benzene and chloroform.

Trimethylamine carbonyl iodoplatinite hydriodide, $COPtI_2,NMe_3,HI$, crystallises in oblique-angled, orange-yellow tables, melts at 95° without decomposition, and is readily soluble in water, by which, however, it is slowly decomposed.

When a solution of carbonyl chloroplatinite in concentrated hydrochloric acid is gradually treated with a 10—20 per cent. solution of potassium thiocyanate until the precipitate first formed is redissolved, a double salt of the composition $COPt(CNS)_2,KCNS$, separates in the cold, in small, yellow needles. This is readily soluble in alcohol, and the solution, on warming with water, becomes red, gas being evolved, a like result being obtained when the salt is dissolved in aqueous potassium cyanide or thiocyanic acid. The double salt is also readily prepared in the crystalline state by adding carbonyl iodoplatinite to an aqueous solution of potassium thiocyanate; the crystals dissolve when the mixture is warmed, and on evaporation platinum thiocyanate and carbonic oxide are obtained, owing to a decomposition of the carbonyl thiocyanoplatinite present in the double salt.

Carbonyl thioplatinite, $COPtS$, is formed as a brown precipitate, resembling platinum sulphide in appearance, when the hydrochloric acid solution of the chloroplatinite is treated with hydrogen sulphide. The compound has little stability, decomposes when placed in a vacuum, burns with a slight explosion when heated at 300—400°, with the production of platinum, sulphur, carbonic anhydride, and sulphurous anhydride, and is insoluble in the ordinary solvents. Potassium cyanide reacts with it, liberating carbonic oxide, and nitric acid decomposes it, with the evolution of carbonic anhydride and nitrous fumes. Under no conditions could carbon oxysulphide be obtained from it, heating at 100—200° in a current of hydrogen leading only to the liberation of carbonic oxide and hydrogen sulphide. On dissolution in ammonium sulphide, it yields a very unstable, acidic compound, which can also be obtained by carefully adding carbonyl iodoplatinite to a solution of sodium sulphide, and to which the formula H_2COPtS_2 is provisionally assigned.

Schützenberger failed to prepare an oxygen derivative of carbonyl platinite by the action of alkalis on the chloroplatinite. A compound of this nature, having possibly the composition $COPtO$, is, however, obtained when the hydrochloric acid solution of the chloroplatinite is stirred into a solution of sodium or ammonium acetate acidified with acetic acid; the mixture at first becomes violet in colour, and then deposits a bluish-black, flocculent precipitate, which, after washing with dilute acetic acid, and subsequently with water, is free from chlorine, and gives a rapid evolution of carbonic oxide on treatment with potassium cyanide. The precipitate dissolves in concentrated hydrochloric acid forming a yellow solution of carbonyl chloroplatinite, reacts with caustic alkalis or baryta, in accordance with the equation $COPtO + 2NaHO = Pt + Na_2CO_3 + H_2O$, and, though stable in a vacuum, or even on gently warming, decomposes with slight explosion at 300—400° into platinum and carbonic anhydride.

So far, all attempts to isolate carbonyl platinite $(COPt)_x$ have been unsuccessful; the authors, however, intimate their intention to undertake further experiments with a view to its isolation.

W. P. W.

Iridio-ammonium Compounds. By W. PALMAER (*Ber.*, **24**, 2090—2097).—In addition to the iridium pentamine compounds already described by the author (this vol., p. 402), derivatives corresponding to the "roseo-" cobaltic compounds have also been prepared. As these are almost colourless, the prefix "roseo-" is unsuitable, and the author therefore proposes for them the term *aquopentamine* compounds, on account of the fact that they differ from the pentamine compounds by containing an additional molecule of water.

In order to prepare the aquopentamine salts, a method is employed similar to that given by Jörgensen for the corresponding rhodium salts. Silver oxide alone is insufficient, and even when caustic potash is employed, the solution must be boiled for several hours.

Iridium aquopentamine chloride, $Ir(NH_3)_5OH_2Cl_3$, is obtained by mixing 5 grams of the pentamine trichloride with $1\frac{1}{2}$ times the calculated quantity of potash, and 50 c.c. of water, and boiling for five hours. The slight precipitate is filtered off, the filtrate partially frozen, and mixed with 30 c.c. of fuming hydrochloric acid. The precipitate thus produced is washed with cold hydrochloric acid (22 per cent.), and subsequently with alcohol, redissolved in water, and again precipitated with concentrated hydrochloric acid. It separates from a concentrated solution in crystalline aggregates resembling those of ammonium chloride, has a sp. gr. of 2·494 at 15°, and on heating at 100° loses water forming iridiopentamine chloride. It dissolves in 1·2—1·5 parts of water; the solution gives a yellow, crystalline precipitate with chloroplatinic acid, and on the addition of sodium pyrophosphate in small quantity yields a white, amorphous precipitate, which dissolves on further addition of the reagent, and then separates out again in irregular, crystalline scales. With chlorine-water, it gives an intense violet coloration, which changes successively to dark-blue, pale-blue, bluish-green, and green, and becomes brown on the addition of ammonia.

Iridioaquopentamine bromide, $Ir(NH_3)_5OH_2Br_3$, is obtained in a similar manner to the chloride, hydrobromic acid being substituted for hydrochloric acid. It is a crystalline compound, has a sp. gr. of 3·022 at 20·1, dissolves in 4 parts of water, and loses water at 100°, with formation of the pentamine salt. With potassium ferricyanide, its solution gives a precipitate consisting of reddish-brown aggregates of crystals, and with sodium pyrophosphate, behaves exactly like the chloride.

Iridium aquopentamine nitrate, $Ir(NH_3)_5OH_2(NO_3)_3$, is prepared by the addition of nitric acid to a solution of the hydroxide obtained by boiling a pentamine compound with aqueous potash, and is a crystalline precipitate consisting of microscopic, rhombic prisms. It dissolves in 10 parts of water at 17°, has a sp. gr. of 2·46 at 18°, and in its behaviour towards potassium ferricyanide and sodium pyrophosphate resembles the bromide. When heated at 100°, it loses water, forming *iridium pentamine nitrate*, $Ir(NH_3)_5(NO_3)_3$, which requires 349 parts of water at 16° for complete solution, has a sp. gr. of 2·51 at 18·3°, yields a crystalline precipitate with platinic chloride, auric chloride, and barium dithionate, and gives a violet coloration with chlorine.

The aqueous solution of iridium aquopentamine nitrate is partially converted into the pentamine salt on boiling, and the reverse reaction

takes place on boiling a solution of the pentamine nitrate. A similar behaviour was observed by Jörgensen with the corresponding rhodium compounds.
H. G. C.

Mineralogical Chemistry.

Kallilite, a New Nickel Ore. By H. LASPEYRES (*Zeit. Kryst. Min.*, **19**, 12—17).—A specimen of a mineral described as antimonial nickel glance, from the Friedrich mine, at Schönstein, on the Sieg, gave on analysis the following results :—

S.	Sb.	As.	Bi.	Fe.	Co.	Ni.	Total.
14·39	44·94	2·02	11·76	0·28	0·89	26·94	101·22

For this mineral the author proposes the name of *bismuth antimonial nickel glance* or *kallilite.* The mineral is an amorphous mixture of 1 mol. arsenical nickel glance, NiAsS, 13 mols. of antimonial nickel glance, NiSbS, and 2 mols. of bismuthic nickel glance, NiBiS. This last substance has, however, not been met with in a pure state.
B. H. B.

Sychnodymite, a New Cobalt Ore. By H. LASPEYRES (*Zeit. Kryst. Min.*, **19**, 17—21).—A mineral obtained from the Kohlenbach mine, at Eiserfeld, near Siegen, was found by the author to be a cobalt compound corresponding with polydymite, and he has given to it the name of sychnodymite. On analysis, the mineral yielded :—

S.	Cu.	Fe.	Co.	Ni.	Total.
40·33	17·23	0·82	35·64	5·74	99·76

B. H. B.

Korynite from Siegen. By H. LASPEYRES (*Zeit. Kryst. Min.*, **19**, 8—12).—In 1887, Hensler described a new nickel ore from the Storch und Schöneberg mine, near Siegen. According to the analysis he published, this mineral possessed the interesting composition of a normal sulphantimonite of nickel. On analysing similar material, the author obtained the following results :—

S.	Sb.	As.	Bi.	Fe.	Co.	Ni.	Total.
16·22	42·93	10·28	0·68	0·40	1·13	28·91	100·55

The mineral is therefore a perfectly normal antimonial nickel glance (ullmannite), NiSbS, with an appreciable, but variable, isomorphous admixture of arsenical nickel glance (gersdorffite), NiAsS.
B. H. B.

Falkenhaynite from Joachimsthal. By F. v. SANDBERGER (*Jahrb. f. Min.*, 1891, i, Mem. 274—276).—In 1890 R. Scharizer described and analysed a new mineral from Joachimsthal, which he named falkenhaynite. A specimen that has been in the author's possession since 1850 is found on analysis to be identical with falkenhaynite. The author points out that this mineral so closely resembles in composition the annivite of Brauns that the two minerals might well be included under one name. The difference between the two minerals is that antimony predominates in falkenhaynite, whilst arsenic and bismuth predominate in annivite. Both minerals are interesting links between bournonite and bismuth-copper ore.

B. H. B.

Gahnite and Columbite from Delaware Co., Pennsylvania. By F. A. GENTH (*Zeit. Kryst. Min.*, **19**, 85—86; from *Proc. Acad. Nat. Sci. Philadelphia*, 1889, 50—52).—Dark-green crystals of *gahnite* found with muscovite, quartz, albite, and garnet in a felspar quarry gave on analysis the following results:—

Al_2O_3.	ZnO.	CuO.	MnO.	FeO.	MgO.	Total.	Sp. gr.
57·22	38·14	0·06	0·70	3·55	0·26	99·93	4·587

The author also gives an analysis of some crystals of columbite found in Mineral Hill Township, Delaware Co., Pennsylvania.

B. H. B.

Monazite from Sweden. By C. W. BLOMSTRAND (*Zeit. Kryst. Min.*, **19**, 109; from *Geol. Fören. Förh.*, **11**, 379).—Under the name of *kararfvite*, Rodominsky distinguished the monazite from Nya Kararfvet on account of its large percentage of fluorine (4·35 per cent.). An analysis of this mineral made by the author proves it to be nothing more than an impure common monazite.

At Holma, in the parish of Luhr, monazite occurs in compact masses of a yellowish-brown colour. The mineral has a sp. gr. of 5·125, and on analysis yielded the following results:—

P_2O_5.	SiO_2.	ThO_2.	Ce_2O_3.	La_2O_3.	Y_2O_3.	FeO.
26·59	2·16	10·39	29·62	26·43	2·54	0·75

CaO.	PbO.	H_2O.	Total.
0·88	0·31	0·52	100·19

B. H. B.

Ochrolite from Pajsberg. By G. FLINK (*Zeit. Kryst. Min.*, **19**, 96—97; from *Ofver. Sv. Vet. Akad. Förh.*, 1889, 5—13).—This mineral gave on analysis the following results:—

PbO.	Sb_2O_3.	Cl.
76·52	17·56	7·72

Formula: $Pb_4Sb_2O_7 + 2PbCl_2$. The mineral crystallises in the rhombic system, and is isomorphous with heliophyllite.

B. H. B.

Formula of Axinite. By A. KENNGOTT (*Jahrb. f. Min.*, 1891, i, Mem. 267).—On calculating the analyses of axinite from Cornwall and from Bourg d'Oisans given by J. E. Whitefield (*Jahrb. f. Min.*, 1891, i, 44), the author obtains the formula $2(Ca_3Al_2O_6,Si_3O_6) + H_2B_2O_4,SiO_2$. A recalculation of Rammelsberg's analysis leads to a similar result.

B. H. B.

Gadolinite and Homilite. By W. PETERSSON (*Jahrb. f. Min.*, 1891, i, Ref. 372—374; from *Ofver. kongl. Vetenskaps Ak. Forhandl.*,

45, 179).—The author gives analyses of gadolinite from seven Scandinavian localities. The general formula deduced from these analyses is $R''_3(R^{vi}_2)Si_2O_{10}$. Microscopic examination showed, however, that in each case the mineral had undergone more or less alteration.

Homilite also undergoes alteration, and consequently the older analyses are worthless for the determination of the composition of unaltered homilite. Quite pure material obtained from the Norwegian soda-syenite gave on analysis the following results:—

H_2O.	Na_2O.	CaO.	FeO.	Fe_2O_3.	Ce_2O_3.	Al_2O_3.	B_2O_3	SiO_2.	Total.
0·79	0·75	29·54	16·74	0·88	0·24	2·72	(16·51)	31·83	100·00

The formula is thus $Ca_2FeB_2Si_2O_{10}$. B. H. B.

Garnet from Kedabek, in Caucasia. By W. Müller (*Jahrb. f. Min.*, 1891, i, Mem. 272—273).—Very fine specimens of garnet are found in the vicinity of Siemens' Copper Works at Kedabek. The garnet occurs in limestone, and is used as a flux for copper smelting. In cavities in the massive mineral, yellow garnet crystals occur, measuring 4·5 cm. in length. On analysis, they yielded:—

SiO_2.	CaO.	Al_2O_3.	Fe_2O_3.	Ignition.	Total.
39·23	35·95	22·73	1·76	0·14	99·81

The mineral is thus a typical lime-aluminium garnet.

B. H. B.

Mesolite from Co. Antrim. By J. S. Hyland (*Jahrb. f. Min.*, 1891, Ref. 400—401; from *Proc. Roy. Dublin Soc.*, 1890, 411—419).—An acicular zeolite from decomposed basalt from Kenbane Head, 2 miles west of Ballycastle, Antrim, gave on analysis the following results:—

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	Na_2O.	H_2O.	Total.	Sp. gr.
46·50	27·55	2·59	13·28	10·10	100·02	2·26

This corresponds with a mixture of 9 of natrolite and 2 of scolezite. The mineral is therefore galactite. B. H. B.

Zircon from Australia. By A. Schmidt (*Zeit. Kryst. Min.*, **19**, 56—58).—In a collection of Australian minerals presented by M. v. Hantken to the University of Budapest, the author has detected some rounded crystals of zircon with an unusually perfect cleavage. On analysis, the crystals gave the following results:—

ZrO_2.	SiO_2.	Total.	Sp. gr.
67·31	33·42	100·73	4·695

B. H. B.

Spherulitic Rocks from Co. Down. By J. S. Hyland (*Jahrb. f. Min.*, 1891, i, Ref. 399—400; from *Proc. Roy. Dublin Soc.*, 1890, 420—437).—Spherulitic rocks are met with at three places in the Mourne Mountains. The rock occurring at Newcastle is porphyritic with felspar and rounded quartz. On analysis, it gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
(70·01)	13·79	1·88	0·51	1·43	0·72	6·90	3·69	1·07	100·00

B. H. B.

Organic Chemistry.

Electrolysis of Metallic Thiocyanates, and the Decomposition of Alkaline Thiocyanates. By L. K. Frankel (*Chem. Centr.*, 1891, i, 615; from *Proc. Chem. Sect. Frankland Inst.*, February, 1891).—When a concentrated aqueous solution of ammonium or potassium thiocyanate is subjected to a weak voltaic current (1·5 c.c. of hydrogen and oxygen evolved per one minute), a yellow precipitate is finally formed which Bunge (*Ber.*, **3**, 297) and Lidoff (*Ber.*, **17**, 252 Ref.) name pseudothiocyanogen. The author has observed the odour of sulphur compounds at the same time.

Mercury and gold may be completely deposited from their solutions in potassium and ammonium thiocyanates, as also cadmium, although the latter metal is obtained as a spongy mass. In the case of palladium, nickel, cobalt, and zinc, the metals are primarily deposited from the solution, but later they are redissolved, owing possibly to the formation of an alkaline cyanide, the solvent action of which is not interfered with. Iron and manganese are but partially precipitated, and the deposited metal is so liable to oxidation that it cannot be exposed to the air without suffering change. Arsenic is not deposited at all. Lead is completely precipitated, but partly as sulphide. With antimony, bismuth, and tin, no very satisfactory results were obtained.

The author considers it probable that Miller's Canarin (*D. Pat. Chem. Centr.*, 1885, 925; also Abstr., 1885, 107) is identical with pseudothiocyanogen, but that the precipitate obtained by the electrolysis of a solution of ammonium thiocyanate is not pseudothiocyanogen. J. W. L.

Polymeride of Trimethylacetonitrile. By M. Freund and F. Lenze (*Ber.*, **24**, 2161—2167).—The colourless liquid boiling at 159—160° which is obtained in the preparation of trimethylacetonitrile from tertiary butyl iodide (compare Abstr., 1890, 1388) has the empirical formula C_5H_9N, but vapour density determinations by Meyer's method have shown that its molecular formula is $C_{10}H_{18}N_2$. When heated with concentrated hydrochloric acid at 100°, it is decomposed into trimethylacetic acid, butylamine, and ammonia; it is also decomposed by alcoholic potash with formation of butylamine, but trimethylacetic acid could not be detected in the reaction product. On reduction with sodium and alcohol, it yields two bases, which seem to have the composition $C_4H_{11}N$ and $C_6H_{15}N$ respectively.

F. S. K.

Compound of Alcohol and Sodium Bisulphide. By L. Demont (*J. Pharm.*, **23**, 544—547).—If a mixture of anhydrous mono- and poly-sulphides of sodium is placed in absolute alcohol, the liquid

gradually assumes a yellow colour, and a slight, although clearly perceptible, rise in temperature may be noted. The mixture is heated gradually to boiling, allowed to cool, and filtered from the excess of sulphide. On adding perfectly dry ether, an abundant, slightly crystalline precipitate is produced. If the ether is not perfectly dry, beautiful, crystalline needles first appear, followed by the less crystalline deposit above. The precipitate first formed with moist ether appears to take water of crystallisation, and when the ether has thus been rendered dry, the granular precipitate follows. The precipitate is very hygroscopic. When rapidly drained, placed over sulphuric acid, or heated at 100°, it loses about 40 per cent. of its weight. The compound thus obtained was analysed, and corresponds with the formula $C_2H_6O + 9NaS$. The original precipitate would be sensibly C_2H_6O,NaS.
J. T

Action of Phosphorus Oxychloride on Ethyl Silicates and Silicon Ethoxychlorides. By H. N. Stokes (*Amer. Chem. J.*, **13**, 244—253).—Silicon ethoxytrichloride, $SiCl_3{\cdot}OEt$, reacts with excess of phosphorus oxychloride at 180° to form silicon tetrachloride, ethyl chloride, and a white, amorphous substance which does not contain free silicic acid, and which gives on analysis numbers corresponding with the formula $SiP_2O_6Cl_2$. Silicon oxychloride is not formed. The author considers that this substance is a chloride of silicopyrophosphoric acid, possibly of the constitution $O{=}Si<\genfrac{}{}{0pt}{}{O{\cdot}POCl}{O{\cdot}POCl}>O$, and that it is formed according to the equation $4SiCl_3{\cdot}OEt + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4EtCl$. If the ethoxytrichloride is in excess, the reaction is similar, but the silicophosphoryl chloride formed is of different composition. Neither the acid nor its salts could be isolated.

Silicopyrophosphoryl chloride, $SiP_2O_6Cl_2$, is a white, bulky, hygroscopic substance, freely soluble in alcohol and water. In contact with moist air, it loses hydrochloric acid, and when heated it gives off first phosphorus oxychloride and then phosphorus pentoxide, leaving finally a vitreous residue consisting of silica embedded in a matrix, probably of the compound SiO_2,P_2O_5. At 100° it is completely decomposed by phosphorus pentachloride into silicon tetrachloride and phosphorus oxychloride. A cold aqueous solution from which the chlorine has been removed by excess of silver nitrate yields, in order, on the addition of ammonia, silver pyrophosphate, silver orthophosphate, and silica.

The reaction of phosphorus oxychloride with the other silicon ethoxychlorides is essentially similar:—

$$2SiCl_2(OEt)_2 + 2POCl_3 = SiCl_4 + SiP_2O_6Cl_2 + 4EtCl.$$
$$4SiCl(OEt)_3 + 6POCl_3 = SiCl_4 + 3SiP_2O_6Cl_2 + 12EtCl.$$

Ethyl orthosilicate reacts with phosphorus oxychloride according to the equation $Si(OEt)_4 + 2POCl_3 = SiP_2O_6Cl_2 + 4EtCl$.

Hexethyl disilicate reacts with phosphorus oxychloride at 100° with the formation of ethyl chloride and a silicophosphoryl chloride much like that described above, but different in composition.

A mixture of the ethoxychlorides formed by heating the hexethyl disilicate with silicon tetrachloride at 200° reacted with phosphoric oxychloride with the formation of silicon tetrachloride, ethyl chloride, a silicophosphoryl chloride, and silica. No silicon oxychloride was formed. JN. W.

Attempt to Prepare Tertiary Butylcarbinol. By M. FREUND and F. LENZE (*Ber.*, **24**, 2150—2161).—The compound obtained by treating tertiary amylamine hydrochloride with silver nitrite (compare Abstr., 1890, 1388) is not tertiary butylcarbinol as it was at first supposed, but is identical with the dimethylethylcarbinol, $CMe_2Et\cdot OH$, previously described by Wischnegradsky (Abstr., 1878, 393); the formation of this compound from the tertiary amine can be explained by assuming that the tertiary butylcarbinol first produced undergoes an intramolecular change analogous to that which takes place in the conversion of pinacones into pinacolines. F. S. K.

Sulphur Compounds in Ohio Petroleum. By C. F. MABERY and A. W. SMITH (*Amer. Chem. J.*, **13**, 233—243; compare Abstr., 1890, 350).—In the commercial process of refining petroleum the sulphur compounds are extracted by treatment with concentrated sulphuric acid. The "sludge acid" thus obtained, on dilution and treatment with slaked lime, yielded a semi-solid mass, from which, by distillation with steam, a colourless oil was obtained containing 14·97 per cent. of sulphur. This oil was distilled first under a pressure of 150 mm. and subsequently under a pressure of 100 mm., and the following main fractions were collected:—

Fraction ...	70–76°	80–90°	98–101°	135–145°	148–155°	185-200°
Sulphur, per cent.	2·60	7·34	18·23	15·52	16·44	14·21

The fractions containing sulphur formed compounds with mercuric chloride, those of lower boiling point giving crystalline substances, and those of higher boiling point viscous oils, which solidified after a time or when recrystallised from benzene. Platinum compounds of the type $R_2S,PtCl_4$ were readily formed. All the fractions combined energetically with bromine.

The products collected below 101° at 100 mm. pressure were redistilled under ordinary pressure. The fractions distilling below 125° combined with hydrobromic acid to form oily substances; the product thus obtained from the fraction boiling at 80—90° was found to be monobromheptane. Analysis of the mercury compounds obtained from the fraction boiling at 110° and upwards revealed the presence of methyl, ethyl, propyl, and butyl sulphides.

The fraction from the sulphuric acid extract boiling at 80—90° under 150 mm. pressure consisted of higher sulphides, together with oily substances free from sulphur. The sulphides were separated from the latter by means of the mercury compounds, which were precipitated by alcoholic mercuric chloride as viscous or crystalline compounds easily decomposable by hydrogen sulphide. Propyl sulphide was probably present in this fraction. The fractions of higher boiling point were identified as ethylpentyl, normal and isobutyl, and hexyl sulphides; butylpentyl and pentyl sulphides were probably also present. The fractions of higher boiling point than hexyl sulphide were not examined.

In order to further investigate the nature of the lighter oils, crude "naphtha distillate," boiling below 150°, was treated with aqueous mercuric chloride, and the precipitate thus obtained decomposed by hydrogen sulphide in the presence of alcohol. The sulphur oils separated from the alcoholic solution on the addition of water, and on distillation under atmospheric pressure collected in fractions which were identified as methyl, ethyl, ethylpropyl, and normal propyl sulphides.

Small quantities of sulphur compounds were obtained directly from crude petroleum. JN. W.

l.-Sorbitol. By E. FISCHER and R. STAHEL (*Ber.*, **24**, 2144).—Further experiments have shown that the hexahydric alcohol obtained by the reduction of l.-gulose (this vol., p. 677) is, in fact, the optical isomeride of ordinary sorbitol. When the syrupy alcohol, purified by means of its benzal derivative, is dissolved in warm 90 per cent. alcohol (7 parts), small needles are deposited in the course of about eight days; this crystalline product contains a large quantity of water, resembles ordinary sorbitol very closely in appearance, and, after having been kept for three days over sulphuric acid under reduced pressure, it melts at about 75° and has the composition $C_6H_{14}O_6 + \frac{1}{2}H_2O$. It can only be distinguished from ordinary sorbitol by its optical properties; it is feebly lævorotatory in presence of borax, whereas ordinary sorbitol is feebly dextrorotatory ($[\alpha]_D^{20} = 1·4°$) under the same conditions. F. S. K.

Configuration of Grape Sugar and its Isomerides. By E. FISCHER (*Ber.*, **24**, 1836—1845).—The experimental evidence afforded by a study of the members of the sugar group is in such complete accordance with the theory of the asymmetric carbon atom that it is possible, even with our present knowledge, to employ this theory as a basis for the classification of these substances.

The theory accounts for the existence of 16 isomerides having the structure of grape sugar, but this number is reduced to 10 in the case of those derivatives of grape sugar, the molecule of which is symmetrical; in the table (next page), taken from Van't Hoff and Herrmann's "Die Lagerungen der Atome im Raume," these 16 different modifications are shown, the forms numbered 11 to 16 being identical with those numbered 5 to 10 in the case of the hexahydric alcohols and dicarboxylic acids.

Now, in attempting to determine, with the aid of observed facts, which of these 16 forms should be assigned to grape sugar, it is necessary in the first place to consider the case of saccharic acid. Of this acid the two optically active forms of opposite sign are known, and, in addition, it has been shown that d.-saccharic acid can be obtained on the one hand from d.-glucose, and on the other from the stereochemical isomeride d.-gulose (this vol., p. 677); it follows,

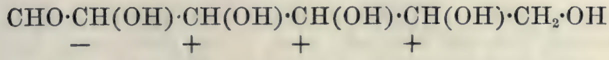
				11	12	13	14	15	16
				+	+	+	+	+	−
				+	+	+	−	−	+
				+	−	−	+	−	−
+	+	−	−	−	+	−	−	−	−
+	−	+	−	−	+	−	−	−	−
+	−	+	−	+	−	−	+	−	−
+	+	−	−	+	+	+	−	−	+
				+	+	+	+	+	−
1	2	3	4	5	6	7	8	9	10

therefore, that the configurations of the two saccharic acids must be represented by two among the forms numbered 5 to 10, because these are the only modifications which could be produced from two stereochemically isomeric sugars. Since two of these forms, namely, those numbered 7 and 8, are optically inactive, they may at once be dismissed from consideration; those numbered 6 and 10 may also be excluded, as is shown by the following arguments:—Glucose and mannose differ from one another only in this, that the arrangement of groups around the asymmetrical carbon atom, marked in the accompanying formula with an asterisk, is not the same in the two compounds—

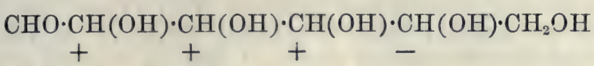
$$OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot \overset{*}{C}H(OH)\cdot CHO.$$

This is also the only difference between gluconic acid and mannonic acid, sorbitol and mannitol, saccharic acid and mannosaccharic acid. The facts on which this statement is based, and which all lead to the same conclusion, are:—(1.) Mannose and glucose yield the same osazone. (2.) l.-Mannonic acid and l.-gluconic acid are both produced from arabinose by means of hydrogen cyanide. (3.) When fructose is reduced with sodium amalgam, it is converted into a mixture of mannitol and sorbitol. (4.) Mannonic acid and gluconic acid can be converted one into the other at will by heating with quinoline. (5.) All attempts to resolve gluconic acid and mannonic acid into two components have been unsuccessful. If, therefore, saccharic acid or, what comes to the same, sorbitol has the configuration numbered either 6 or 10, mannosaccharic acid or mannitol must have the configuration 7 or 8; but the latter are the optically inactive systems and must, therefore, be excluded because both mannitol and mannosaccharic acid are optically active. It follows from these arguments that d.- and l.-saccharic acid can only have the configurations numbered 5 and 9, and since it is immaterial which is designated with +, and which with −, the configuration numbered 5 may be assigned to d.-saccharic acid, and that numbered 9 to l.-saccharic acid.

Now, there are two aldoses corresponding with d.-saccharic acid, having the configurations:—



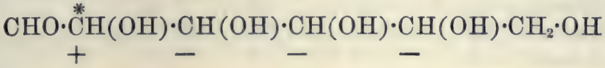
$$\mathrm{CHO{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}CH_2{\cdot}OH}$$

and 

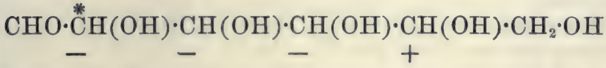
$$\mathrm{CHO{\cdot}\underset{+}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}CH_2OH}$$

respectively; in order to decide which of these formulæ represents d.-glucose and which d.-gulose, it is necessary to study some facts regarding arabinose and xylose.

In the first place, arabinose can be converted into l.-glucose, whilst xylose, under the same conditions, yields l.-gulose; there remains, therefore, a choice between the two formulæ :—

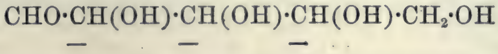


$$\mathrm{CHO{\cdot}\underset{+}{\overset{*}{C}H(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}CH_2{\cdot}OH}$$

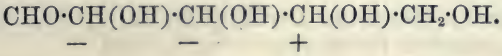
and 

$$\mathrm{CHO{\cdot}\underset{-}{\overset{*}{C}H(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}CH_2{\cdot}OH}$$

for l.-glucose and l.-gulose. If the asymmetrical carbon atom which is marked with an asterisk, and which only becomes asymmetric by synthesis, is taken away, it will be seen that there remain for xylose and arabinose the following two formulæ :—

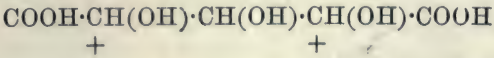


$$\mathrm{CHO{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}CH_2{\cdot}OH}$$

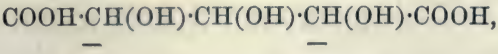
and 

$$\mathrm{CHO{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{-}{CH(OH)}{\cdot}\underset{+}{CH(OH)}{\cdot}CH_2{\cdot}OH.}$$

Again, according to the theory, there may be eight isomeric pentoses having the constitution of arabinose and xylose, but this number is reduced to four when the molecule becomes symmetrical; there are, therefore, only four pentahydric alcohols of the constitution $\mathrm{OH{\cdot}CH_2{\cdot}[CH(OH)]_3{\cdot}CH_2{\cdot}OH}$ and four trihydroxyglutaric acids. Of the latter there are two optically active modifications, namely :—



$$\mathrm{COOH{\cdot}\underset{+}{CH(OH)}{\cdot}CH(OH){\cdot}\underset{+}{CH(OH)}{\cdot}COOH}$$

and 

$$\mathrm{COOH{\cdot}\underset{-}{CH(OH)}{\cdot}CH(OH){\cdot}\underset{-}{CH(OH)}{\cdot}COOH,}$$

and two inactive modifications, which probably could not be distinguished from one another. It is possible, therefore, to decide which of the above two formulæ represents arabinose and which xylose by observing the optical properties of the corresponding pentahydric alcohols or dicarboxylic acids; experiments have shown, in a very decided manner, that arabinose has the configuration represented by the first, and xylose that represented by the second formula.

Arabitol, prepared from arabinose, is lævorotatory in presence of borax (compare Fischer and Stahel, this vol., p. 667); this is also so in the case of the trihydroxyglutaric acid prepared from arabinose, as will be shown below. Xylitol, obtained from xylose, is, on the other hand, optically inactive (*loc. cit.*) even in the presence of borax, and so is the trihydroxyglutaric acid prepared from xylose (see below). Now, since the hydroxy-acids, if optically active at all, invariably possess a high specific rotatory power, it may be assumed with confidence that these derivatives of xylose really are optically inactive and that the configuration just assigned to xylose is the correct one.

The configurations of the members of the hexose group are easily deduced from the above considerations and may be expressed as follows:—

Aldoses: $CHO\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$.

d.-Glucose	–	+	+	+
l.-Glucose	+	–	–	–
d.-Gulose	+	+	+	–
l.-Gulose	–	–	–	+
d.-Mannose	+	+	+	+
l.-Mannose	–	–	–	–

As regards galactose, there remains a choice between four configurations, as will be seen by a comparison with the formulæ of mucic acid and with those of allomucic acid.

Ketoses: $CH_2(OH)\cdot CO\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$.

d.-Fructose	+	+	+
l.-Fructose	–	–	–

The monocarboxylic acids, $COOH\cdot[CH(OH)]_4\cdot CH_2\cdot OH$ have the same configurations as the corresponding aldoses.

Aldehyde-acids: $COOH\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CHO$.

Glucuronic acid	+	+	+	–

Alcohols: $OH\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$.

d.-Mannitol	+	+	+	+
l.-Mannitol	–	–	–	–
d.-Sorbitol	–	+	+	+
l.-Sorbitol	+	–	–	–

Dicarboxylic acids:
$COOH\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot COOH$.

d.-Saccharic acid	–	+	+	+
l.-Saccharic acid	+	–	–	–
d.-Mannosaccharic acid	+	+	+	+
l.-Mannosaccharic acid......	–	–	–	–

In addition to the above, two other members of this group, namely, mucic acid and isosaccharic acid, are known. The former is optically inactive, and when treated with pyridine is converted into an inactive allomucic acid; these two isomerides have in all probability the configurations (– + – +) and (– – + +).

A second isomeride of mucic acid, which is, however, optically active, has been obtained by treating galactonic acid with quinoline and oxidising the product with nitric acid; this modification has probably the configuration (+ − + +) or (− + − −). There remain then for isosaccharic acid only the two configurations (+ − − +) and (− + + −).

The views expressed above are of course tenable only when it is assumed that the theory of the asymmetric carbon atom is true and, further, that no stereochemical intramolecular change occurs in those reactions by which trihydroxyglutaric acid and saccharic acid are produced from xylose and arabinose. Of the facts mentioned above in support of these views, the conversion of xylose into optically inactive trihydroxyglutaric acid and the proof that this acid is not identical with the compound obtained from arabinose have yet to be described.

Inactive trihydroxyglutaric acid, $C_5H_8O_7$, is formed when xylose is oxidised with nitric acid of sp. gr. 1·2 ($2\frac{1}{2}$ parts) at 40° as described by Kiliani in the oxidation of arabinose; it is isolated by means of its calcium salt, the yield of which is 18 grams from 30 grams of the sugar. It crystallises from hot acetone in well-defined, colourless plates, melts at 145·5° (corr.), decomposes at a higher temperature, and is very readily soluble in water and hot alcohol, but much more sparingly in warm acetone, and almost insoluble in chloroform and ether. It is optically inactive, and does not act on Fehling's solution, but it reduces ammoniacal silver nitrate on warming; in a solution of the acid, lead acetate and barium acetate produce precipitates, that obtained with barium acetate being soluble in excess of the reagent. The calcium salt is very sparingly soluble in water. The *potassium* salt, $C_5H_6O_7K_2$, is very readily soluble, and remains as a syrup on evaporating its aqueous solution; this syrup solidifies after some time, and can then be recrystallised from water, from which it separates in well-defined, hexagonal plates or prisms containing 2 mols. H_2O, which are expelled at 130°. This acid is easily distinguished from the isomeride obtained from arabinose by its melting point, optical inactivity, and the composition of its potassium salt. When a 10 per cent. solution of the acid is heated with phenylhydrazine, the hydrazide commences to be deposited in about half an hour; it crystallises in colourless plates, sinters together at about 175° when quickly heated, melts at about 210° with decomposition, and is very sparingly soluble in hot water and alcohol. That inactive trihydroxyglutaric acid contains a normal carbon chain is proved by the fact that, on reduction with hydriodic acid and amorphous phosphorus, it is converted into glutaric acid (m. p. 95—96°).

The specific rotatory power of the trihydroxyglutaric acid prepared from arabinose is $[\alpha]_D = -22·7°$ at 20°; the rotatory power undergoes no change in the course of 24 hours. The above views on the configuration of the members of the sugar group render it possible to foresee a whole series of reactions which can be carried out by known methods; as an example, the reduction of d.-mannosaccharic acid may be quoted. If this compound has the configuration assigned to it above, it is immaterial which of the two carboxy-groups is reduced;

in other words, only one acid, namely, d.-mannonic acid, can be produced. Experiments have proved the correctness of this supposition; when the double lactone of d.-mannosaccharic acid is treated with sodium amalgam in slightly acid solution, the only product is d.-mannonic lactone. F. S. K.

Influence of Inactive Substances on the Rotatory Power of Very Dilute Solutions of Grape Sugar. By N. Wender (*Ber.*, **24**, 2200—2203).—A series of experiments has shown that Landolt's formula $c = 0{\cdot}9434\alpha$ (*Optische Drehungsvermögen*, 1879, 182) holds good in the case of grape sugar even in very dilute solutions (0·1—0·4 gram in 100 c.c.), and also that the presence of carbamide and other inactive constituents of urine has no effect on the rotatory power of such dilute solutions. F. S. K.

Rotatory Power of Levulose and Invert Sugar. By B. Tollens (*Ber.*, **24**, 2000).—Ost (this vol., p. 1000) has overlooked the fact that Parcus and Tollens (*Annalen*, **257**, 165) have found that the rotatory power of levulose is greater than hitherto accepted. The values given by both authors are in close agreement.

W. P. W.

Chemical Composition of the Membrane of Plant Cells. By E. Schulze (*Ber.*, **24**, 2277—2287; see also Abstr., 1889, 916; 1890, 1456).—The constituents of the plant cell membrane are divided into those which are easily extracted with dilute mineral acids and those which are difficult to extract. The author has already described six celluloses of different origin, converted them into glucoses by the method described by Flechsig, and finally in all cases obtained grape sugar from them. He has now obtained three other cellulose preparations from pine wood (*Picea excelsa*), from rye-straw (*Secale cereale*), and from red clover (*Trifolium pratense*), and has treated them in the same way, and obtained the sugar in a crystalline condition.

The wood cellulose was prepared by the sulphite method, and before use was extracted with 4 per cent. hydrochloric acid. The other cellulose preparations were prepared by extracting the finely broken material with ether, dilute aqueous soda, 4—5 per cent. hydrochloric acid, then with F. Schulze's reagent (cold, dilute nitric acid and potassium chlorate), and finally washed with dilute ammonia, water, alcohol, and ether. These three celluloses, on hydrolysis, also yielded grape sugar, which was crystallised first from water, then from alcohol, and finally from methyl alcohol, and was identified by its specific rotation, behaviour towards yeast, and by yielding saccharic acid when heated with nitric acid.

Lastly, they have examined the cellulose preparation from sesame seeds, and have also obtained grape sugar from it. Ten celluloses have now been obtained which give grape sugar on hydrolysis, and an eleventh (cotton cellulose) has been examined by Flechsig (*Zeit. physiol. Chem.*, **7**, 523).

To determine if these celluloses yielded other glucoses besides grape sugar, the mother liquors were examined. In no case was galactose detected. Only in the crude crystallisable product from rye-straw cellulose was a small quantity of a pentaglucose detected by means of hydrochloric acid and phloroglucinol. Mannose was obtained from many of the preparations in considerable quantity; it was first detected in those prepared from coffee beans (*Ber.*, **23**, 2582). A second experiment was made with a carefully prepared coffee cellulose. The preparation was obtained by extracting with 4 per cent. hydrochloric acid, then treated with F. Schulze's reagent, and washed with dilute ammonia, water, alcohol, and ether. It yielded a syrup which contained considerable quantities of d.-mannose. Mannose is also obtained from the cellulose from cocoa and sesame seeds.

Besides these constituents, a substance is also present in the most carefully purified cellulose preparations which is convertible into xylose. The presence of the latter is shown by the violet colour produced on boiling the preparation with hydrochloric acid and phloroglucinol. Those celluloses which colour most strongly when treated in this way yield a large proportion of furfuraldehyde.

The author proposes to restrict the name cellulose to that constituent of the cell wall which is not dissolved by dilute mineral acids and alkalis, and scarcely attacked by F. Schulze's reagent, but is soluble in ammoniacal copper oxide, and yields grape sugar on hydrolysis. If, however, "cellulose" be employed as a group-name, he proposes to call the above compound dextroso-cellulose, and the cellulose-like compound which yields mannose on hydrolysis is called mannoso-cellulose. Those constituents of the cell wall which dissolve easily in dilute mineral acids, with formation of glucose, he calls hemicelluloses, and distinguishes them by the names of galactane, arabane, xylane, according as they yield galactose, arabinose, or xylose. A product which yields both galactose and arabinose he proposes to call galacto-arabane, &c. E. C. R.

Hexamethylenamine. By L. HARTUNG (*J. pr. Chem.* [2], **43**, 597—598).—Hexamethylenamine is not split up easily by hydrochloric acid into ammonia and formaldehyde as heretofore supposed; a considerable quantity of methylamine is formed, and can be separated by alcohol from the ammonium chloride and paraformaldehyde. Strong nitric acid acts on hexamethylenamine in glacial acetic acid very violently with evolution of nitrous oxide, ammonia and methylamine being also formed. Nitrous acid acts on it in glacial acetic acid evolving nitrogen and nitric oxide, and forming a white, amorphous substance which is decomposed by potash with formation of ammonia and methylamine. Sulphurous acid, acting on it in hot absolute alcohol, produces a white compound, $C_5H_{11}N_3SO_3$; when benzene is substituted for alcohol, the resulting compound is $C_6H_{12}N_4SO_2$, which loses half its SO_2 at 60—70°. Ethyl chloracetate acts on hexamethylenamine at 100°, with separation of alcohol, to form the compound $C_{14}H_{25}ClN_8O$, of which the platinochloride was analysed; if the reaction takes place in hot alcohol, hexamethylenamine hydrochloride separates, whilst the above compound is precipitated from the filtrate on addition of ether. A. G. B.

Biguanide. By F. EMICH (*Monatsh.*, **12**, 5—22).—The products of decomposition of biguanide, obtained by the action of sulphuric acid of sp. gr. 1·47 at 200°, alcoholic potash at 100°, and red-hot lime, were comparatively simple, such as carbonic anhydride, ammonia, cyanic acid, and cyanamide (Emich, Abstr., 1883, 973, and 1889, 1060). The author now finds that the decomposition of the base, by boiling it with baryta water, does not proceed so far as in the above mentioned cases, carbamide and guanidine being produced. Similarly from methylbiguanide are formed methylcarbamide, carbamide, guanidine, and, perhaps, methylguanidine; whilst phenylbiguanide gives phenylcarbamide, carbamide, phenylguanidine, and guanidine.

Diethylbiguanide, $NEt_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2$, is obtained by heating at 130°, for some hours, a mixture of equal parts of diethylamine hydrochloride and dicyanodiamide. The product is treated with chloroform, which dissolves the diethylbiguanide and any remaining diethylamine, the solution evaporated, the residue dissolved in water, and the solution thus obtained treated with copper sulphate and potash, whereby the red copper compound is precipitated. From this, by solution in dilute sulphuric acid and precipitation of the copper with hydrogen sulphide, diethylbiguanide sulphate, $NEt_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2,H_2SO_4 + 3H_2O$, was obtained as a white precipitate on the addition of alcohol to the clear filtrate. It crystallises from water in clusters of small, flat prisms, is insoluble in ether, has an acid reaction, sinters at 185°, and melts with decomposition at 197°. On heating at 100° in a closed tube for 3—4 hours with baryta water, it is decomposed with formation of diethylamine.

β-Diphenylbiguanide, $NPh_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2$, is obtained by heating together diphenylamine hydrochloride and dicyanodiamide either alone or in alcoholic solution. It has a strongly alkaline reaction, crystallises in white needles, melts with decomposition at 160—162°, and on treatment with dilute nitric acid gives a *nitrate*, $C_{14}H_{15}N_5,HNO_3$, which has a neutral reaction, and melts with blackening and evolution of gas at 201—203°. The corresponding acid sulphate, $(C_{14}H_{15}N_5)_2,3H_2SO_4$, crystallises from water in spherical aggregates of needles, and furnishes diphenylamine when heated with lime.

G. T. M.

Guanidine. By F. EMICH (*Monatsh.*, **12**, 23—28).—*Guanidine picrate*, $CH_5N_3,C_6H_2(NO_2)_3\cdot OH$, is precipitated in a pure form when an aqueous solution of picric acid is added to a moderately concentrated solution of a salt of guanidine. The picrate is only sparingly soluble in water (1 part in 2630 at 9°), alcohol, and ether, and this property makes it available for the quantitative estimation of the base. It crystallises in very characteristic forms, does not melt at 280°, burns at a higher temperature, and when struck does not explode.

On treating guanidine carbonate with a solution of sodium hypobromite, two-thirds of its nitrogen was evolved in the gaseous form, in accordance with the equation $NH{:}C(NH_2)_2 + 3O = HCNO + 2H_2O + N_2$, the cyanic acid being itself undecomposed by hypobromite.

Solutions of guanidine carbonate containing phosphates and other inorganic salts necessary to bacterial life were not changed by *Penicillium glaucum* or by putrefying urine; but the compound itself is not powerfully antiseptic. G. T. M.

Oximes. By V. Meyer (*Annalen*, **264**, 116—122).—It is a curious fact that the oximes of low melting point have a much more strongly marked acid character than their isomerides of high melting point; if, for example, bromacetophenone (1 mol.) or methoxyacetophenone (1 mol.) is treated with hydroxylamine hydrochloride (3 mols.) and sodium hydroxide (9 mols.), an alkaline solution is obtained from which, on the addition of a large quantity of water, the oxime of high melting point is deposited in an almost pure condition, whilst the isomeride remains in solution, and is only precipitated on the addition of acids; this difference of behaviour can be made use of for the separation of the two isomerides when only small quantities are present.

Chloralaldoxime, $CCl_3\cdot CH\colon N\cdot OH$, can be easily prepared by treating a mixture of chloral hydrate (1 mol.) and hydroxylamine hydrochloride (4 mols.) with a quantity of water just sufficient to moisten the crystals throughout, and then warming gently, when a colourless oil separates from the solution; after warming for a short time, the oil is washed with water, then cooled in ice, and the crystalline product repeatedly washed with water and dried between blotting paper. It forms large, compact prisms, melts at 39—40°, boils without decomposition when heated in small quantities, and is readily soluble in alcohol and ether, but insoluble in water; it is not easily obtained in crystals from its solutions, and its vapours have a very irritating action on the eyes. It is decomposed by concentrated alkalis with almost explosive violence; when treated with dilute soda, it yields hydrogen cyanide, hydrogen chloride, carbonic anhydride, and a colourless, resinous compound, but the formation of chloroform, formic acid, and hydroxylamine could not be observed; on evaporation with concentrated hydrochloric acid, the oxime suffers decomposition, and there remains a crystalline residue of hydroxylamine hydrochloride.

Acetoxime combines readily with the chlorides of benzene-, paratoluene-, and naphthalene-β-sulphonic acid in presence of soda, yielding crystalline compounds which will be described in another paper; analogous derivatives of benzophenone oxime cannot be easily obtained. F. S. K.

Constitution of Aliphatic Ketones and the Action of Sodium on Acetone. By P. C. Freer (*Amer. Chem. J.*, **13**, 308—322).—The author discusses at length the constitution of ethyl acetoacetate and acetone.

Powdered sodium dissolves in a solution of dry ethyl acetate in dry ethyl ether, and the resulting product yields nothing but ethyl acetoacetate when treated with hydrochloric acid. This would seem to point to the intermediate formation of Frankland's hypothetical sodium derivative of ethyl acetate (*Jahrb.*, 1865, 204).

A comparison of the properties of tetric acid, $C_5H_6O_3$ (Abstr., 1888, 1272), with those of ethyl acetoacetate seems to show that hydroxyl is present in the former, but not in the latter. Tetric acid forms a crystalline compound with phenylhydrazine, and is not reduced by sodium amalgam. The sodium salt, $NaC_5H_5O_3 + 3H_2O$, crystallises in plates, which lose their water of crystallisation in a vacuum over sulphuric acid. The anhydrous salt is stable at 190°. Sodium tetrate does not react with ethyl iodide, but the silver salt yields ethyl tetrate, an oil boiling at 176° under a pressure of 50 mm. Ethyl tetrate is insoluble in water and cold aqueous soda, but soluble in alcohol and ether. It is hydrolysed by potash, showing that the ethyl group is attached to oxygen. Tetric acid reacts with warm acetic anhydride to form a neutral, colourless oil, boiling at 178° under 50 mm. pressure. The oil, which has the composition of acetotetric acid, $C_7H_8O_4$, is reconverted into tetric acid by aqueous potash or alcoholic hydroxylamine.

The author endorses the view that in carbon compounds containing both metal and oxygen, the metal is united to the carbon only indirectly through the oxygen. This would seem to involve a difference in constitution between ethyl acetoacetate and its sodium derivative. That this is the case is shown by the fact that the latter unites with ethyl cinnamate to form a crystalline additive product, whilst the former does not. Further details of this reaction are to be published.

The formation of sodium acetonate (Abstr., 1890, 956) has been further studied. The theoretical amount of hydrogen is displaced by the sodium, and a small amount of a condensation product, probably mesityl oxide, is formed (compare following abstract). JN. W.

Action of Ethyl Chlorocarbonate on Acetone-sodium. By P. C. FREER and G. O. HIGLEY (*Amer. Chem. J.*, **13**, 322—326; compare preceding abstract).—Excess of acetone is added in an atmosphere of hydrogen to powdered sodium (1 gram) covered with ether, and the calculated amount of ethyl chlorocarbonate (4·7 grams) is gradually introduced. As soon as the violent reaction is complete, the process is repeated until a sufficient quantity of the product has accumulated. The sodium chloride which separates out is then extracted with water, and the ethereal residue is evaporated, leaving a yellow oil, the greater part of which boils at 128°, and appears, from analysis and vapour-density determinations, to be an isomeride of ethyl acetoacetate. The purified oil is colourless and insoluble in water, but miscible with alcohol and ether in all proportions. It does not react with phenylhydrazine or ferric chloride. Bromine combines with it slowly in the cold to form additive products, but in sunlight acts as a substituting agent. On boiling with dilute hydrochloric acid, it is decomposed quantitatively into carbonic anhydride, alcohol, and acetone. The authors suggest the formula

$$CH_2{:}CMe{\cdot}O{\cdot}COOEt$$

for the new substance, and conclude that in acetone-sodium the metal is combined with oxygen. JN. W.

"Acetone-potash" and "Acetone-soda." By W. VAUBEL (*J. pr. Chem.* [2], **43**, 599—600).—When acetone is heated with solid potassium hydroxide, a crystalline substance separates on the surface of the liquid after about five minutes, and gradually increases in quantity. When it is dried by filter paper, washed free from excess of acetone by light petroleum, and left in a desiccator, it forms a white powder which is very hygroscopic, and readily loses acetone. The analyses of this substance agree with the formula $KHO + COMe_2$.

"Acetone-soda" can be prepared in like manner; it has not yet been investigated. A. G. B.

Action of Chlorine on Methyl Ethyl Ketone. By D. VLADESCO (*Bull. Soc. Chim.* [3], **5**, 142—149).—Methyl ethyl ketone is chlorinated in a reflux apparatus by a slow stream of dry chlorine free from hydrogen chloride. The progress of the reaction is determined by the amount of hydrogen chloride collected in a flask containing distilled water, connected to the condenser, twenty-four hours being required in cloudy weather to form the monochloro-derivative. Hydrogen chloride and excess of chlorine are expelled from the product of the reaction by a current of carbonic anhydride, and after washing with dilute solution of potassium carbonate, it is dried over calcium chloride and fractionated.

From the fraction boiling at 114—116°, methyl chlorethyl ketone is separated by distillation, under reduced pressure, as a colourless liquid of an irritating, ethereal odour. It boils at 115° under a pressure of 758 mm., has a vapour density of 3·8, and a sp. gr. at 0° of 1·032.

By distillation, under reduced pressure, of the fraction boiling at 164—166°, a methyl dichlorethyl ketone is obtained as a colourless liquid boiling at 165° under a pressure of 753 mm.; its vapour density is 4·8, and its sp. gr. at $0° = 1·096$.

Both the above chlorinated derivatives are insoluble in water, but dissolve in alcohol and ether; they form crystalline compounds with sodium hydrogen sulphite, and are reduced by nascent hydrogen to methyl ethyl ketone. Sodium hydroxide acts on monochloromethyl ethyl ketone to form dimethylketole (compare Abstr., 1890, 1234), so that its constitution is probably $COMe{\cdot}CHClMe$, whilst dichloromethyl ethyl ketone, on treatment with potassium hydroxide, yields diacetyl, and is probably $COMe{\cdot}CCl_2Me$. T. G. N.

Preparation of Triacetin. By C. BÖTTINGER (*Annalen*, **263**, 359—360).—Triacetin can be very conveniently prepared by heating glycerol (20 c.c.) with acetic anhydride (10 c.c.) and finely divided potassium hydrogen sulphate (50 grams) until the reaction is at an end and the two liquids have formed a homogeneous mixture, and then gradually adding a further quantity (20 c.c.) of acetic anhydride to the boiling solution, when a very energetic reaction takes place. After boiling for a short time, the solution is decanted from the salt, mixed with ether, filtered, the ether evaporated, and the product purified by fractional distillation. Triacetin passes over at 264—268°, and a smaller quantity of diacetin at about 285°. F. S. K.

Cyanisonitrosoacetic Acid. By H. G. Söderbaum (*Ber.*, **24**, 1988—1992).—The acid previously described as furazancarboxylic acid (this vol., p. 827) closely resembles Wolff and Gans' so-called cyanonitrosoacetic acid in properties (this vol., p. 897), and the only points of difference between the author's acid and that of Wolff and Gans (stability in a desiccator and stability on boiling with caustic alkali) have been removed by a further examination of a fresh quantity of the acid under the conditions employed by Wolff and Ganz. The *copper* salt, $C_3N_2O_3Cu + 4H_2O$, crystallises in six-sided, or seemingly four-sided, tablets of rhombic character, is rather sparingly soluble in cold water, and, like the silver and calcium salts, agrees in all respects with the corresponding salt of Wolff and Gans' acid. W. P. W.

Alloisomerism: De-halogenisation of Ethyl Salts of α-β-Halogenised Acids. By A. Michael and O. Schulthess (*J. pr. Chem.* [2], **43**, 587—596).—Hitherto support for the Van't Hoff-Wislicenus hypothesis has been sought for by de-halogenising halogen-alkyl compounds (Abstr., 1889, 236, 576). These compounds are difficult to prepare in a state of purity, and the authors hope that a study of the ethyl salts of α-β-halogenised acids will prove more productive of results.

When zinc acts on a cooled solution of ethyl α-β-dibromopropionate in ether, zinc bromide is formed, and by shaking the solution with water to remove this salt, evaporating off the ether, and distilling, a good yield of ethyl acrylate is obtained. It was noted that ethyl acrylate can dissolve zinc bromide, and that the above reaction will not take place in absolute ether, a very small quantity of water being necessary.

Ethyl α-β-dibromobutyrate is obtained by saturating an alcoholic solution of dibromobutyric acid (m. p. 87°) with hydrogen chloride; it is an oil which boils at 110·5—111° (21 mm.) and does not dissolve in water. By acting on it with zinc in an ethereal solution at the ordinary temperature, ethyl crotonate was obtained, which, on hydrolysis, yielded crotonic acid of m. p. 72°.

Claus (Abstr., 1883, 43) found that when ethyl dibromosuccinate is treated with zinc and ethyl bromide, the latter is not acted on, while 1 or 2 atoms of zinc enter into combination with the acid, without removing bromine, and syrupy liquids containing zinc are formed. The authors have repeated this experiment, and find that when the ethyl bromide is dry no reaction takes place, but on the addition of a drop of water the action is violent, and zinc bromide and ethyl fumarate (equal molecular proportions) are formed, and can be separated by shaking with water. Claus' syrupy liquids were solutions of zinc bromide in ethyl fumarate (compare above). The same results were obtained when ether was substituted for ethyl bromide; no reaction occurred if the ether was absolute. No ethyl maleate could be detected. Ethyl allodibromosuccinate was similarly treated, but only ethyl fumarate was obtained; this is contrary to the Van't Hoff-Wislicenus hypothesis, according to which ethyl maleate should have been formed. The temperature of the above reactions did not rise above 25°, and the solutions remained neutral.

Ethyl citradibromopyrotartrate, obtained by acting on ethyl citraconate in ether with bromine in daylight, boils at 164° (22 mm.).

Ethyl itadibromopyrotartrate is similarly prepared in a chloroform solution; it is a colourless oil, and boils at 158° (19 mm.) The former of these salts yields mesaconic acid when the product of the action of zinc on its moist ethereal solution is saponified, while the latter yields itaconic acid under the same conditions; the temperature did not rise above 25° during the reaction. According to the Van't Hoff-Wislicenus hypothesis, citraconic acid should be formed when ethyl citradibromopyrotartrate is dehalogenised; but the authors found no trace of it.

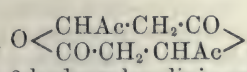
When ethyl α,β-trichlorobutyrate (b. p. 101·5; 17 mm.) is dehalogenised in the way described above, ethyl α-chlorocrotonate (m. p. 172—173°) is formed, and no ethyl allo-α-chlorocrotonate, which should have been formed, according to the Van't Hoff-Wislicenus hypothesis (compare Liebermann, this vol., p. 832). A. G. B.

Preparation of Ethereal Salts of β-Ketonic Acids. By J. HAMONET (*Bull. Soc. Chim.* [3], **5**, 23; compare Abstr., 1890, 235, 1891, 41).—Bouveault states that the author's method for preparing alkyl β-ketonates yields only salts of the general formula

$$R\cdot CH_2\cdot CO\cdot CHR'\cdot COOR'';$$

the latter replies that if these salts are first acted on by sodium, and subsequently by an alkyl iodide or an acid chloride, compounds corresponding with the formula $R\cdot CH_2\cdot CO\cdot CR'R''\cdot COOR'''$ are obtained.
T. G. N.

Hydroxylevulinic Acid and Acetylacrylic Acid. By L. WOLFF (*Annalen*, **264**, 229—260).—It has been previously shown (Abstr., 1887, 464) that when the β-bromolevulinic acid obtained from the dibromide of angelicalactone is treated with sodium carbonate, it yields β-hydroxylevulinic acid and acetylacrylic acid; some additional facts regarding these two compounds and their derivatives are given in this paper.

The *lactide*,  $O<\begin{matrix}CHAc\cdot CH_2\cdot CO\\CO\cdot CH_2\cdot CHAc\end{matrix}>$, is gradually deposited in slender needles when β-hydroxylevulinic acid is kept over sulphuric acid; it is also formed, with elimination of water, carbonic anhydride, and diacetyl, when the acid is heated at 150°. It separates from boiling alcohol and chloroform in colourless needles, sinters together at 238°, melts at 240° with decomposition, and is insoluble in sodium carbonate, and only sparingly soluble in cold water, alcohol, chloroform, ether, and carbon bisulphide; it is slowly reconverted into the acid by boiling water.

When β-hydroxylevulinic acid is heated with phenylhydrazine at 100°, diacetylosazone (m. p. 244°) is formed with evolution of carbonic anhydride and ammonia.

Isonitrosohydroxyvaleric acid, $OH\cdot N:CMe\cdot CH(OH)\cdot CH_2\cdot COOH$, prepared by treating β-hydroxylevulinic acid with hydroxylamine in alkaline solution at the ordinary temperature, crystallises from water in colourless, lustrous plates or prisms, melts at 145° with evolution of carbonic anhydride, and is very readily soluble in hot water, but only moderately easily in cold water, and sparingly in ether, benzene, chloroform, carbon bisulphide, and light petroleum; in its aqueous solutions ferric chloride produces a red coloration which disappears on the addition of hydrochloric acid. The *calcium* salt, $(C_5H_8NO_4)_2Ca$, crystallises in needles, is moderately easily soluble in water, and seems to contain 1 mol. H_2O. The *silver* salt, $C_5H_8NO_4Ag$, crystallises from water in lustrous needles, and is gradually decomposed by boiling water. When the acid is distilled, it is completely decomposed, yielding as principal products tetramethylpyrazine (*loc. cit.*) and diacetyldioxime; these two compounds combine together to form a colourless, crystalline substance having the composition

$$OH\cdot N\colon CMe\cdot CMe\colon N\cdot OH,2C_4N_2Me_4,$$

which separates from boiling benzene in slender needles, melts and sublimes at 178°, and is readily soluble in warm ether and alcohol, but only sparingly in cold water, chloroform, benzene, and carbon bisulphide; it is decomposed into its constituents by acids, alkalis, and boiling water.

Acetylacrylic acid is best prepared by heating β-bromolevulinic acid (1 part) with anhydrous sodium acetate (1 part) and glacial acetic acid ($1\frac{1}{2}$ parts) for half an hour at 100°; the yield of the pure acid is 90 per cent. of the theoretical. The *ethyl* salt, $C_5H_5O_3Et$, prepared from the silver salt, or from ethyl β-bromolevulinate, is a colourless oil of sp. gr. 1·057 at 0°, and boiling at 206—207°; it is readily soluble in ether and alcohol, but only sparingly in water, and its vapours are very irritating. The *oxime*, $OH\cdot N\colon CMe\cdot CH\colon CH\cdot COOH$, separates from hot water in colourless, cauliflower-like aggregates, melts at 206° with decomposition, and is readily soluble in alcohol and moderately easily in hot water and ether, but only sparingly in cold water, carbon bisulphide, benzene, and chloroform; in its aqueous solution, ferric chloride produces a red coloration. The *barium* salt, $(C_5H_6NO_3)_2Ba$, crystallises from water in small plates, and is very readily soluble in warm water; in its aqueous solution, silver nitrate produces a flocculent, sparingly soluble precipitate, and ferric chloride a red precipitate which dissolves in hot water with an intense red coloration. The *hydrazone*, $N_2HPh\colon CMe\cdot CH\colon CH\cdot COOH$, crystallises from boiling water in yellow needles, melts at 160° with decomposition when heated quickly, and is readily soluble in alcohol, ether, and boiling water; when heated at its melting point, it yields a basic substance which is probably identical with the phenylmethylpyridazone described by Ach (Abstr., 1889, 70).

When acetylacrylic acid is boiled with barium hydroxide, it is decomposed into acetone, oxalic acid, and two other acids, one of which is crystalline and readily soluble in ether; the other is a thick, dark syrup, sparingly soluble in ether. The crystalline *acid* has the composition $C_9H_8O_5$, melts at 207°, and is readily soluble in alcohol and hot water, but only sparingly in chloroform and benzene; its *calcium* salt is readily soluble, but its *silver* salt, $C_9H_6O_5Ag_2$, is very sparingly soluble in boiling water.

αβ-Dibromolevulinic acid, $C_5H_6O_3Br_2$, is formed when acetylacrylic acid is treated with bromine in ice-cold chloroform solution; it crystallises from hot benzene in lustrous needles, melts at 108°, and is very readily soluble in ether, alcohol, and hot benzene, but only moderately easily in cold water and chloroform, and sparingly in light petroleum and carbon bisulphide.

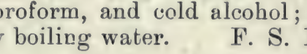
When acetylacrylic acid is reduced with sodium amalgam, it is converted into levulinic acid and hydroxyvaleric acid.

α-Bromolevulinic acid, $C_5H_7O_3Br$, is produced, together with dibromolevulinic acid (m. p. 114—115°) and small quantities of β-bromolevulinic acid (m. p. 59°), when acetylacrylic acid is heated with hydrobromic acid at 100° for some hours. The two compounds are separated by means of chloroform, in which the monobromo-derivative is readily soluble. It crystallises from carbon bisulphide in lustrous plates, melts at 79—80°, and is readily soluble in ether and alcohol, but only moderately easily in water, benzene, and boiling carbon bisulphide, and sparingly in light petroleum.

α-Hydroxylevulinic acid, $C_5H_8O_4$, prepared by boiling the preceding compound with water, crystallises from warm water in colourless needles, sinters together at 100°, and melts at 103—104°; it is readily soluble in water and alcohol, but only moderately easily in ether and chloroform, and very sparingly in carbon bisulphide, benzene, and light petroleum; it reduces Fehling's and ammoniacal silver nitrate solutions. The calcium salt is amorphous, and the silver salt is unstable. The *lactide*, $C_{10}H_{12}O_6$, is formed when the acid is heated at about 100°; it crystallises from boiling alcohol in slender needles, melts at 263° with decomposition, and is only sparingly soluble in water, ether, carbon bisulphide, chloroform, and cold alcohol; it is gradually reconverted into the acid by boiling water. F. S. K.

Action of Ammonia and Aniline on Ethyl α-Acetoglutarate.

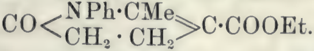
By W. O. EMERY (*Amer. Chem. J.*, **13**, 351—354; compare this vol., p. 544).—A mixture of ethyl α-acetoglutarate (1 vol.) and concentrated alcoholic ammonia (2 vols.), after standing 24 hours in the cold, and distilling off the unchanged portion, deposits white crystals of a substance which may be regarded as the lactam of ethyl α-amido-α-ethylideneglutarate,



$CO<\begin{matrix}NH\cdot CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot COOEt$.

It melts at 156°, and is soluble in chloroform and ether.

When aniline is substituted for the ammonia, the residue left after the distillation crystallises on the addition of ether. The white substance thus obtained may be regarded as the lactam of ethyl α-anilido-α-ethylideneglutarate,

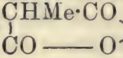
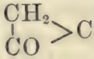


$CO<\begin{matrix}NPh\cdot CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot COOEt$.

It melts at 196°, and is easily soluble in chloroform, but with difficulty in ether. JN. W.

Tetric Acid, Oxytetric Acid, and their Homologues.

By P. WALDEN (*Ber.*, **24**, 2025—2039).—The compounds obtained by

Demarçay (Abstr., 1880, 625) from the monobromo- and dibromo-substitution products of ethyl alkylacetoacetates, and described under the above title, have been since then repeatedly investigated, without any certain conclusion being reached (Abstr., 1883, 730, 1085; 1884, 834). The two most recent suggestions with regard to tetric acid are those of Moscheles (Abstr., 1888, 1272), who regards it as a lactone of the formula  $\left.\begin{array}{l}\mathrm{CHMe{\cdot}CO}\\ \mathrm{CO}\text{——}\mathrm{O}\end{array}\right>\mathrm{CH_2}$, and of Wolff (this vol., p. 416), who proposes the formula  $\left.\begin{array}{l}\mathrm{CH_2}\\ \mathrm{CO}\end{array}\right>\mathrm{CMe{\cdot}COOH}$. In order to ascertain whether the acid behaves as a true carboxylic acid, the author has determined the conductivity of the normal sodium salt, which, according to Ostwald's experiments, is a certain criterion of the basicity of the acid. The results obtained with tetric acid and its homologues agree well with the supposition that they are monobasic acids; for the sake of comparison, the author determined the conductivity of certain substances which behave in some respects as acids, namely, Kiliani's saccharin, which has a constitution similar to that given by Moscheles for tetrinic acid, and of ethyl acetoacetate, ethyl ethylacetoacetate, trihydroxyquinoline, and α-naphthol, all of which proved, as expected, to be very bad conductors, whilst the tetric acids have a conductivity five times as great as that of the fatty acids. On the other hand, it was found that ethyl orthonitrobenzoylmalonate, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH(COOEt)_2}$ (Abstr., 1885, 263), gave numbers as high as a true carboxylic acid, and is indeed so strong an acid that it decomposes solutions of potassium acetate, succinate, &c. Hence the question of the presence of the carboxyl group in tetric acid, &c., must still be regarded as open.

Oxytetric acid and its homologues show conductivity constants which agree with the supposition that they are dicarboxylic acids, and further investigation has shown that they are in reality alkyl-substituted fumaric acids. Thus oxytetric acid is identical with mesaconic acid, oxypentic acid with ethylfumaric acid, and so on. In the same manner, the acids described by Demarçay as hydroxytetric acid, &c., and which differ from the oxy-acids in containing two additional hydrogen atoms, are identical with the alkylsuccinic acids, hydroxytetric acid being methylsuccinic acid, hydroxypentic acid ethylsuccinic acid, and so on.

The preparation of alkylfumaric acids by Demarçay's method gives a comparatively good yield, and the operations are fairly simple. The bromination of the substituted ethyl acetoacetate is best carried out in ethereal solution, cooling well with ice-cold water, the dibromo-compound remaining on evaporation of the ether, gradually adding to a mixture of 5 mols. of potash with half its weight of alcohol, with continuous shaking and cooling. After warming for half-an-hour at 100°, volatile products are removed by a current of steam, and the residue acidified and extracted repeatedly with ether. The crude product which remains on evaporating the ether is purified by several crystallisations from water, with addition of animal charcoal. To convert the substituted fumaric acids thus obtained into the corresponding succinic acids, the best reducing agent is granulated zinc and dilute sulphuric acid.

Tetric acid and its next higher homologues are obtained by heating the monobromo-derivatives of the substituted ethyl acetoacetates under pressure at 100° for six hours, washing the product with a mixture of benzene and light petroleum, and recrystallising from water. The higher homologues are formed simply by allowing the brominated ethereal salts to remain, or more quickly by warming them in an open flask. H. G. C.

Electrolysis of Cobalt Salts of Oxalic Acid. By F. Kehrmann and N. Pickersgill (*Ber.*, **24**, 2324—2326).—The authors have isolated the green salt obtained by the electrolysis of cobaltous oxalate dissolved in potassium oxalate, and find it to have the composition $3K_2C_2O_4 + Co_2(C_2O_4)_3 + 6H_2O$, and to be identical with the salt obtained by dissolving cobaltic hydroxide in a concentrated solution of acid potassium oxalate (Abstr., 1887, 220). Cobalt oxalate is dissolved in a boiling saturated solution of potassium oxalate, and electrolysed in a platinum dish with constant addition of acetic acid, so as to maintain the mixture faintly acid. When the green colour has reached a maximum intensity, the solution is fractionally precipitated with alcohol; cobaltous potassium oxalate and potassium oxalate are at first precipitated. The mother liquor is then precipitated with a large volume of alcohol, and the green precipitate purified by solution in water and reprecipitation with alcohol. It is thus obtained in beautiful, dark-green crystals. The aqueous solution of the salt acts as a strong oxidising agent, and on boiling is decolorised with precipitation of cobaltous oxide salt.

No corresponding compound was obtained on treating nickel potassium oxalate in the same way. Mangano-potassium oxalate gave an intense purple-red solution, but the compound is so unstable that the authors have not yet been able to isolate it. E. C. R.

Determination of the Structure of Fatty Acids by Bromination. By K. Auwers and R. Bernhardi (*Ber.*, **24**, 2209—2233).—The bromination of fatty acids by means of bromine and amorphous phosphorus, in the manner described by Hell, Volhard, and Zelinsky, has frequently been a subject of investigation, and from the facts afforded by the experiments hitherto carried out, the following rules may be laid down:—(1.) Fatty acids yield a bromo-substitution product only when the molecule contains at least one atom of hydrogen in the α-position relatively to the carboxy-group. (2.) When bromination takes place at all, the product is invariably a monobromo-derivative. As these rules are based on very insufficient evidence, the authors have studied the behaviour of a large number of mono- and di-carboxylic acids under the conditions referred to above, and more fully described below; the following statements give a summary of their results:—(1.) All fatty mono- and di-carboxylic acids which contain one or more atoms of hydrogen in the α-position relatively to the carboxy-group are easily brominated, and the size of the molecule does not influence the course of the reaction. (2.) The greatest number of atoms of hydrogen which are substituted by bromine under the normal conditions is equal to the number of carboxy-groups in the molecule of the acid; when, however, a very large excess of the theoretical quantity of bromine is employed, and the duration of the experiment is greatly extended, a comparatively very small quantity of a dibromo-derivative is obtained in the case of acetic, propionic (?), and normal butyric acids. (3.) Dicarboxylic acids, such as malonic acid and glutaric acid, which contain hydrogen atoms in the α-position to both the carboxy-groups, yield dibromo-substitution products; succinic acid and its alkyl derivatives form an exception to this rule (compare following abstract). It must be stated, however, that no experiments were made by the authors to prove that the bromine atom in the substitution product really occupies the α-position to the carboxy-group; that it does so in the case of α-bromisobutyric acid and α-bromopalmitic acid has been already shown by Bischoff, and by Hell and Jordanoff; judging by analogy, it may be assumed, therefore, that this is also true in the case of other fatty acids, especially as substitution takes place only when the acid contains a hydrogen atom in the α-position.

The experiments were carried out as follows:—A quantity of bromine, calculated from the equations:—

$$3C_nH_{2n+1}\cdot COOH + P + 11Br = 3C_nH_{2n}Br\cdot COBr + HPO_3 + 5HBr,$$
$$3C_nH_{2n}(COOH)_2 + 2P + 22Br = 3C_nH_{2n-2}Br_2(COBr)_2 + 2HPO_3 + 10HBr,$$

is gradually added to a mixture of the acid (10—20 grams) and the theoretical quantity of amorphous phosphorus, any considerable rise of temperature being avoided; the mixture is then gradually heated to 90—100°, and small quantities of bromine added, until the evolution of hydrogen bromide ceases; this extra quantity of the halogen is added to compensate for loss during the process. In the case of the monocarboxylic acids, the reaction usually occupies a few hours, but for the conversion of the dicarboxylic acids into dibromo-derivatives 10—15 hours are required. Finally the product is treated with absolute alcohol, and the ethereal salt produced in this way submitted to fractional distillation, or the product is decomposed with water, and the brominated acid purified by the usual methods.

The new compounds obtained in the course of this investigation will be now described.

Ethyl bromocaprylate, $C_{10}H_{19}BrO_2$, is a colourless liquid boiling at 245—247° under the ordinary pressure, and at 170—176° under a pressure of 100°.

Bromolauric acid, $C_{12}H_{23}BrO_2$, is a colourless, crystalline compound melting at 30—31·5°; it is almost insoluble in cold water, and only sparingly soluble in cold light petroleum, but readily in alcohol, benzene, ether, and chloroform. The *ethyl* salt, $C_{14}H_{27}BrO_2$, boils at 172—174° under a pressure of 10·5 mm.

Ethyl bromostearate, $C_{20}H_{39}BrO_2$, melts at 33—34·5°, and is readily soluble in ether, chloroform, light petroleum, and benzene, but only sparingly in cold alcohol, and insoluble in water.

Dibromoglutaric acid (normal), $C_5H_6Br_2O_4$, crystallises from ether in compact prisms, melts at 169—170°, and is readily soluble in ether, glacial acetic acid, and hot water, but almost insoluble in benzene, chloroform, and light petroleum; the *ethyl* salt, $C_9H_{14}Br_2O_4$, boils at about 160° under a pressure of 21 mm.

Dibromo-β-methylglutaric acid, $C_6H_8Br_2O_4$, separates from benzene in crystals melting at 151—152°.

Dibromosebacic acid, $C_{10}H_{16}Br_2O_4$, crystallises in needles, melts at 117·5—119°, and is readily soluble in hot water, alcohol, ether, chloroform, and hot benzene, but only sparingly in cold benzene, and insoluble in water. F. S. K.

Bromination of Succinic Acid and its Alkyl Derivatives. By K. AUWERS and A. IMHÄUSER (*Ber.*, **24**, 2233—2240).—When succinic acid is treated with bromine and amorphous phosphorus in the manner described in the preceding abstract, the principal product is monobromosuccinic acid; only small quantities of the dibromo-acid are produced, even when the succinic acid is treated first at the ordinary temperature, and then for a long time at about 90°, with a quantity of bromine sufficient to convert the whole of the acid into the dibromo-derivative. Glutaric acid, like succinic acid, is only brominated with difficulty in comparison with other dicarboxylic acids; when the acid is heated with bromine at about 90°, the monobromo-derivative is the principal product, but larger or smaller quantities of the dibromo-acid are formed according to the conditions of the experiment; when the mixture is heated at 100°, the principal product is the dibromo-acid, a small quantity of the anhydride of bromocitraconic acid being also produced. The bromoglutaric acid obtained in this way melts at 147°. and is probably identical with citrabromoglutaric acid (m. p. 148°); the dibromo-derivative melts at 150—151°, and seems to be identical with citradibromoglutaric acid (m. p. 150°).

When either of the symmetrical dimethylsuccinic acids is treated with bromine and amorphous phosphorus under various conditions, the principal product is invariably pyrocinchonic anhydride (m. p. 96°); a small quantity of a colourless, crystalline compound melting at 135—160° was also obtained in some of the experiments, but the formation of the monobromo-substitution product, described by Hell and Rothberg (Abstr., 1889, 371), was not observed.

F. S. K.

Monoximes of Succinic Acid. By A. PIUTTI (*Ber.*, **24**, 2287—2290).—Hantzsch has stated that the reason for his work on these compounds (Hantzsch and Cramer, this vol., p. 823) was that the author had retained a formula which represented the nitrogen combined with two carbon atoms in spite of his (Hantzsch's) paper "On the Position in Space of Atoms in Molecules containing Nitrogen" (Abstr., 1890, 348). The author states that his paper here referred to "On a New Synthesis of Asparagin" was laid before the Reale Accademia di Napoli before he had seen Hantzsch's paper.

Since then he has obtained a large number of results which agree with those obtained by Hantzsch, and gives a list of the compounds he has prepared. E. C. R.

Electrolytic Synthesis of Bibasic Acids. By A. CRUM BROWN and J. WALKER (*Annalen*, **261**, 107—128; also *Trans. Roy. Soc. Edin.*, **36**, 211—224).—When an aqueous solution of potassium acetate is electrolysed, the following reactions take place at the anode:—

(1.) $2CH_3{\cdot}COO + H_2O = 2CH_3{\cdot}COOH + O$.
(2.) $2CH_3{\cdot}COO = CH_3{\cdot}CH_3 + 2CO_2$.
(3.) $2CH_3{\cdot}COO = CH_3{\cdot}COOCH_3 + CO_2$.

In a weak solution, the first action predominates; in a concentrated solution, the second. The authors find that strong solutions of potassium ethyl salts of acids of the oxalic series are also decomposed according to equation 2. Thus in the case of potassium ethyl malonate we have $2COOEt{\cdot}CH_2{\cdot}COO = COOEt{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt + 2CO_2$, obtaining in this way succinic acid from its lower homologue malonic acid. In the same way, adipic acid may be obtained from succinic acid, and so the oxalic acid series may be ascended (compare Abstr., 1890, 583).

The electrolysis is conducted in a large platinum crucible (4·8 cm. high, 4·3 cm. across), which serves as cathode. The anode is a stout platinum wire, wound into a spiral, and presenting a surface equal to $\frac{1}{30}$th of the internal surface of the crucible. This ensures a great current density at the anode, which the authors show to be essential to the success of the synthesis. The current employed has a strength of 3—5 ampères and an E.M.F. of 12 volts. The crucible is cooled by a current of water flowing round it. All the potassium ethyl salts examined were found to be excessively soluble in water; the best concentration for electrolysis is 1·5 to 2 parts salt in 1 part water. 25 grams of potassium ethyl malonate could be electrolysed under the above conditions in an hour, giving 9·2 grams of diethyl succinate, equal to 60 per cent. of the theoretical quantity. The synthesis goes equally well with potassium methyl salts.

Besides the ethereal salts formed according to the equation, other ethereal products appear with the higher acids of the series, but these were not investigated.

The succinic and adipic acids obtained in the above manner are identical with those prepared in other ways. The yield of diethyl adipate from ethyl potassium succinate was 35 per cent. of the theoretical. From ethyl potassium adipate, the diethyl salt of ordinary sebacic acid was obtained (yield 20 per cent.), thus proving that sebacic acid is a normal bibasic acid. Similarly, from ethyl potassium glutarate ordinary diethyl suberate was prepared (yield 28 per cent.). Suberic acid is thus also normal.

Ethyl potassium suberate, on electrolysis, yielded the diethyl salt of a new acid, *normal dicarbododecanic acid*,

$$COOH{\cdot}[CH_2]_{12}{\cdot}COOH.$$

The diethyl salt is a crystalline mass melting at 27°. The acid melts at 123°, and is decomposed at high temperatures. It is very slightly soluble in water, soluble in hot alcohol and ether. The alkaline salts are soluble in water; the others are insoluble. Yield 25 per cent.

Another new acid, *normal dicarbodecahexanic acid*,

$$COOH\cdot[CH_2]_{16}\cdot COOH,$$

was prepared similarly from sebacic acid. In this case the electrolytic solution must be warmed to 50° in order that the current may continue to flow, as the diethyl salt which is formed melts only at 43°. The acid melts at 118°, is scarcely soluble in water, slightly soluble in ether, but easily soluble in hot alcohol. Only the alkaline salts are soluble in water. Yield 20 per cent.

The potassium ethyl salts for electrolysis are prepared from the corresponding diethyl salts, which are half saponified by the calculated quantity of alcoholic potash. The alcoholic solution is evaporated to dryness, and the residue taken up with water, the resulting aqueous solution being then shaken out with ether, and evaporated to the proper concentration. The ethereal products of the electrolysis float to the surface as oils, which may be easily separated and purified.

J. W.

Synthesis of Alkyl Derivatives of Succinic Acid. By A. CRUM BROWN and J. WALKER (*Proc. Roy. Soc. Edin.*, **18**, 95—97).—Ethyl potassium methylmalonate (150 grams), on electrolysis (compare preceding abstract), yielded an ethereal product (60 grams) of which half boiled between 194° and 206°.

This fraction was saponified, and the resulting potassium salt converted into acid. The crude acid was freed from a small quantity of oil, and subjected to systematic fractional crystallisation from water. Two acids were thus obtained, both having the composition $C_6H_{10}O_4$. The less soluble acid melted at 193°, the other at 120—121°. From an investigation of their properties, including the electrical conductivity, these acids were found to be identical with anti- and para-*s*-dimethylsuccinic acids (m. p. 194° and 120° respectively).

In like manner, ethyl potassium ethylmalonate yielded, on electrolysis and treatment as above, two isomeric acids of the composition $C_8H_{14}O_4$. On further examination, these proved to be para-symmetrical-diethylsuccinic acid (m. p. 192° with decomposition) and anti-symmetrical-diethylsuccinic acid (m. p. 130°). J. W.

New Isomeride of Mucic Acid and the so-called Paramucic Acid. By E. FISCHER (*Ber.*, **24**, 2136—2143).—The dicarboxylic, just like the monocarboxylic, acids of the sugar group can be partially converted into their stereochemical isomerides by heating them with quinoline, or with an aqueous solution of pyridine; when mucic acid (100 grams), which is almost insoluble in boiling quinoline, is heated at 140° for three hours with water (1 litre) and commercial pyridine (200 grams), it is partially transformed into a new isomeride, which the author names allomucic acid.

Allomucic acid, $C_6H_{10}O_8$, crystallises from water in microscopic needles, melts at 166—171° with decomposition, and is soluble in 10—12 parts of boiling water, but only very sparingly in alcohol; it is optically inactive. It has a lower melting point than mucic acid, from which it differs also in being much more soluble in water. When its aqueous solution is boiled or evaporated, the acid is partially converted into a compound which is identical with the so-called paramucic acid, but which is in reality a lactone acid, as will be shown below. The potassium, sodium, ammonium, and magnesium salts are much more readily soluble in water than the corresponding salts of mucic acid. The *calcium* salt, $C_6H_8O_8Ca$, is obtained when a solution of the acid in water (50 parts) is neutralised with calcium carbonate; on evaporating the filtered solution, the salt is deposited in the form of a crystalline powder, which, when dried at 100°, seems to contain $1\frac{1}{2}$ mols. H_2O, part of which ($\frac{1}{2}$ mol.) is expelled at 130°; the barium and cadmium salts, like the calcium salt, are crystalline and very sparingly soluble in water. The *diphenylhydrazide*, $C_6H_8O_6(N_2H_2Ph)_2$, is deposited in crystals when an aqueous solution of the acid is boiled for an hour with phenylhydrazine; it melts at 213° with decomposition when quickly heated, and is very sparingly soluble in hot water and alcohol. When allomucic acid (1 gram) is heated with concentrated hydrochloric acid (1 gram) and fuming hydrobromic acid (1 gram) at 150° for eight hours, it is converted into dehydromucic acid; d.-mannosaccharic acid can also be transformed into dehydromucic acid by heating its lactone with a mixture of these two acids. When allomucic acid is heated with water and pyridine at 140°, it is partially converted into mucic acid.

The *lactone acid* of mucic acid, hitherto known as paramucic acid, is formed when a solution of mucic acid (30 grams) in water (2 litres) is boiled for 20—30 minutes, and the solution then evaporated to 300 c.c. over the free flame; the crystals of mucic acid (8 grams) are separated from the cold solution by filtration, the filtrate evaporated in a vacuum at about 50° to a thin syrup, and the residue mixed with pure acetone. The solution is again filtered from crystals of the acid, and evaporated over sulphuric acid under reduced pressure; the residue still contains a little acid, produced by the water present in the syrup, but when it is dissolved again in dry acetone, and the filtered solution evaporated over sulphuric acid, the pure lactone is obtained as a thick acid syrup. The compound has not yet been obtained in a crystalline condition, but that it is the lactone acid, and not the dicarboxylic acid, is amply proved by the whole behaviour of the compound, especially by the fact that, on titration with soda at 0°, the quantity of alkali required to neutralise the solution is only half that required when titration is carried out at 100°. When the lactone acid is heated with water at 100°, and the solution then allowed to cool, pure mucic acid is deposited in crystals; the same change takes place, but much more quickly, on warming the lactone acid with concentrated hydrochloric acid or with dilute nitric acid. It is very readily soluble in soda, being thereby converted into sodium mucate; it dissolves freely in alcohol, and is obtained unchanged as a syrup on evaporating the solution over sulphuric acid, but if the alcohol contains inorganic salts or traces of mineral acids, combination takes place between the alcohol and the lactone acid, and a crystalline compound melting at about 175°, which is probably impure ethyl hydrogen mucate, is produced. It is readily reduced by sodium amalgam, yielding an aldehyde acid, from which it is probable that a new monocarboxylic acid of the dulcitol series can be obtained. The *hydrazide*, $C_6H_9O_7{\cdot}N_2H_2Ph$, is deposited, after some time, when phenylhydrazine is added to a moderately concentrated solution of the lactone acid; it crystallises from hot water in colourless plates, melts at 190—195° with decomposition, and is readily soluble in water.

It is clear, from the above facts, that all the present data regarding the solubility of mucic acid in hot water are incorrect; the method of estimating mucic acid, based on its slight solubility in water, is also an inaccurate process, but the errors of estimation would be considerably reduced in this case by evaporating with hydrochloric acid or dilute nitric acid to prevent the formation of the lactone acid.

F. S. K.

Ethyl Ethylenedicarbamate. By O. RHOUSSOPOULOS (*Ber.*, **24**, 2268—2269).—Ethyl ethylenedicarbamate, $C_2H_4(NH{\cdot}COOEt)_2$, is obtained by the action of ethylenediamine on ethyl chlorocarbonate. The reaction takes place at the ordinary temperature and with development of heat. It forms long, white needles, insoluble in cold water, somewhat soluble in hot water, and easily in alcohol and ether. It melts at 113°, and when allowed to crystallise very slowly, it forms thick, monoclinic crystals. Unlike ethyl ethylidenedicarbamate, it is very stable, is not decomposed by soda, and when heated sublimes for the most part without decomposition. Acetic anhydride has no action on it. An attempt to obtain ethylenedicarbimide by distilling it with phosphorus pentoxide failed.

E. C. R.

Constitution of the Tetrole Rings. By G. CIAMICIAN (*Ber.*, **24**, 2122—2127).—The author criticises the views which have recently been put forward by Bamberger (this vol., p. 1032) on the constitution of closed chains of five atoms. In conjunction with Angeli, the author has lately shown that thiophen and its derivatives are more stable, as regards the breaking of the closed chain, than pyrroline and furfurole, whereas according to Bamberger all these compounds have the same character and belong to hexacentric systems, in which the nitrogen atom functions as a pentad, the sulphur and oxygen atoms as tetrads. Even if it be assumed that there are no double linkings in these compounds, there seems to be no reason for supposing that nitrogen functions as a pentad and oxygen and sulphur as tetrads; the three rings may just as well be regarded as tetracentric systems in order to account for their properties in accordance with Bamberger's ideas, and, moreover, the known facts do not warrant the assumption that pyrroline contains pentad nitrogen.

F. S. K.

Pyrone. By J. W. BRÜHL (*Ber.*, **24**, 2450—2455).—Pyrone boils at 105—106° under 13 mm. pressure, melts at 32—33°, solidifies at 31—32°, and has a sp. gr. of 1·1898 at 40·3°/4°. On exposure to air and light, it rapidly becomes coloured, especially when warm. The refractive index was determined by the method recently described by the author (this vol., p. 513), and the numbers obtained at 40·3° for lithium, sodium, and thallium light were $n_{Li} = 1{\cdot}51725$, $n_{Na} = 1{\cdot}52383$, and $n_{Tl} = 1{\cdot}52994$. From these the values for the α, β, and γ hydrogen lines were calculated, that for H_α from n_{Li} and n_{Na} by Cauchy's equation, and those for H_β and H_γ from the numbers observed for French turpentine,

Li.	H_α.	Na.	Tl.	H_β.	H_γ.
1·46202	1·46252	1·46526	1·46836	1·47202	1·47779

by assuming that the differences $n_\beta - n_{Tl}$ and $n_\gamma - n_{Tl}$ stand in the same proportion as $n_{Tl} - n_{Li}$ for the two substances, the refractive indices of pyrone for the three rays being estimated, therefore, as $H_\alpha = 1{\cdot}51821$, $H_\beta = 1{\cdot}53726$, and $H_\gamma = 1{\cdot}54880$. The specific refraction, N, that is, $\frac{n^2 - 1}{(n^2 + 2)d}$, molecular refraction, M, and molecular dispersion, $M_\gamma - M_\alpha$, for pyrone, calculated from these data, are given in the table.

N_α.	N_{Na}.	N_γ.	M_α.	M_{Na}.	M_γ.	$M_\gamma - M_\alpha$.
0·2548	0·2571	0·2673	24·46	24·68	25·66	1·20

Claisen's synthesis of chelidonic acid (this vol., p. 425) affords evidence in favour of the pyrone formula, $CO<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>O$, first proposed by Lieben and Haitinger, but, as pyrone does not form additive compounds or a hydrazone or oxime, further confirmation seemed desirable. This is supplied by the data given, since for a compound of Lieben and Haitinger's formula the molecular refraction for H_α calculated by the author's method (this vol., p. 775) is $M_\alpha = 23{\cdot}89$, and for sodium light calculated from Conrady's constants is $M_{Na} = 24{\cdot}09$, numbers which agree well with the experimental values. The molecular dispersion for a compound of this formula calculated from the data given in the same paper is about 0·90, and the fact that the experimental value is 1·20 affords evidence in favour of the view there expressed, that when a carboxyl radicle is linked to unsaturated carbon atoms the dispersive power is unusually high.

W. P. W.

Action of Chlorine on Benzene in presence of Sulphuric Acid. By ISTRATI and PÉTRICOU (*Bull. Soc. Chim.* [3], **5**, 165—168).—Dry chlorine is passed for six days through a mixture of benzene (200 c.c.) and sulphuric acid (300 c.c.) contained in a reflux apparatus, the temperature being increased from 80° upwards as chlorination proceeds. In addition to franceïnes, which are dissolved by the sulphuric acid, a solid mass of chlorobenzene is obtained, consisting of tetrachlorobenzene (1 : 2 : 4 : 5), pentachlorobenzene, and small quantities of monochlorobenzene and paradichlorobenzene. The author also separated some chlorobenzenesulphonic acid, $C_4H_4Cl{\cdot}SO_3H$, which bears out his theory that the final chloro-derivatives are formed from the action of hydrochloric acid on intermediary chlorosulphonic acids.

T. G. N.

Benzene Hexachlorides. By C. FRIEDEL (*Bull. Soc. Chim.* [3], **5**, 130—138).—The author endeavours to account for the existence of the two isomeric benzene hexachlorides by arguments based on the possible stereochemical constitution of the two substances. The original paper should be consulted. T. G. N.

New Method of Iodation in the Aromatic Series. By ISTRATI (*Bull. Soc. Chim.* [3], **5**, 158—162).—In preparing franceïnes by the action of concentrated sulphuric acid on halogen derivatives of benzene, a migration of the halogen occurs, resulting in the formation of higher derivatives (compare Abstr., 1890, 51), this having also been noticed by Herzig (Abstr., 1882, 46) and by Neumann (Abstr., 1887, 573). The author's process is as follows:—Benzene (1 litre), sulphuric acid, sp. gr. 1·84 (2 litres), are introduced into a reflux apparatus of about 5 litres capacity, and so soon as sulphonation is induced by gentle warmth a corresponding quantity of iodine is added. Iodation begins at 80°, and as it progresses the temperature may be increased to 200°. The author explains the reaction according to the following equations:—(1) $C_6H_5{\cdot}SO_3H + I_2 = C_6H_4I{\cdot}SO_3H + HI$, (2) $C_6H_4I{\cdot}SO_3H + HI = SO_2 + H_2O + C_6H_4I_2$, and this is borne out by the fact that much SO_2 is evolved during the reaction, while the sulphonic acids which exist in quantity at that stage of the process when the diiodo-derivative is formed have almost completely disappeared when the tetraiodo-derivative is produced. In the case of the higher homologues of benzene, great care must be exercised in heating the mixture, or carbonisation ensues. T. G. N.

Iodopentachlorobenzene. By ISTRATI (*Bull. Soc. Chim.* [3], **5**, 169).—Pentachlorobenzene melting at 74° and boiling at 272° (100 grams), sulphuric acid, sp. gr. 1·84 (400 c.c.), and iodine (55 grams) are boiled together during 24 hours; on cooling, a substance is deposited which melts at 130—135°. The supernatant sulphuric acid contains a franceïn. After treatment of the mass with soda and washing with distilled water, the excess of pentachlorobenzene is removed by extracting with hot alcohol, and the residue of iodopentachlorobenzene is purified by recrystallisation from chloroform. The substance forms colourless, silky needles which melt at 207·5—208°, and its solution in chloroform is decomposed by sunlight. T. G. N.

Orthonitrotoluene. By F. STRENG (*Ber.*, **24**, 1987).—Orthonitrotoluene is usually stated to boil at 223°, and to remain liquid at −20°. Pure orthonitrotoluene, free from the para-compound, boils at 218°, solidifies completely at −10·5°, and has a sp. gr. = 1·168 at 15°. W. P. W.

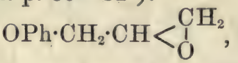
Occurrence of Ethylbenzene in Commercial Xylene. By E. NOELTING and G. A. PALMAR (*Ber.*, **24**, 1955—1958).—The occurrence of ethylbenzene in coal-tar has not hitherto been observed, although the presence of ethyl alcohol in the "first runnings" of the benzene stills has been recorded. In separating paraxylene from coal-tar xylene by Jacobsen's method (this Journal, 1877, i, 600) the authors obtained a hydrocarbon which boiled at 134—138°, and did not crystallise even in a good freezing mixture. On bromination by Friedel and Crafts' method (Abstr., 1886, 229), this gave a mixture of tetrabromoxylene and pentabromethylbenzene, and as a result it was found that two-thirds of the supposed paraxylene consisted of ethylbenzene corresponding with an approximate proportion of 10 per cent. in the crude xylene. All specimens of coal-tar xylene subsequently examined have been found to contain ethylbenzene, although in smaller proportion, and the presence of ethylaniline in commercial xylidine has also been detected. W. P. W.

Colouring Matter of Red Carbolic Acid. By E. FABINI (*Chem. Centr.*, 1891, i, 401, and 448; from *Pharm. Post*, **24**, 41).—If reduced copper be dissolved in pure phenol out of contact with the air, a yellowish-brown solution is formed, which does not become red. If this solution be shaken with 1 part of water, light-brown flakes are precipitated, which are insoluble in alcohol, ether, &c. The phenol containing this compound, *copper diphenyl*, $CuPh_2$, becomes intensively carmine-coloured when treated with a little ammonia and hydrogen peroxide. If the colouring matter be precipitated with water and extracted with ether, the copper diphenyl remaining has not lost weight, but is now darker coloured, owing to some change in composition. If pure phenol be treated with ammonia and hydrogen peroxide, no formation of the red dye occurs; if a knife blade be dipped into this, blood-red streaks will commence to flow from its surface. The author considers that the most probable cause of the partly liquid condition of phenol is the presence of ammonium phenoxide, which is liquid, and the brown colour is attributable to the presence of copper or iron, 0·0001 per cent. of either of these metals being sufficient to cause a dark-brown coloration. Oxygen or bleaching powder acts on ammonium phenoxide with formation of a blue colouring matter, phenocyanin, which is soluble in ether in presence of free acid. The ethereal solution is red, and the residue left on evaporation of the ether dissolves in concentrated sulphuric acid, forming a green solution, the colour becoming, later, less distinctive. This colouring matter is quite distinct from the copper diphenyl, which does not become blue on addition of ammonia. J. W. L.

Action of Epichlorhydrin on Phenols. By T. V. LINDEMANN (*Ber.*, **24**, 2145—2149).—*Phenyl α-chlorohydrin ether*,

$$OPh\cdot CH_2\cdot CH(OH)\cdot CH_2Cl,$$

is formed, together with phenyl glycidol ether (see below), when phenol is heated with epichlorohydrin at 150° for six hours; the two products are separated by distillation with steam, the last-named compound alone being volatile. Phenyl α-chlorohydrin ether is a yellow oil and cannot be distilled even under reduced pressure; when boiled with an aqueous solution of potassium phenate, it is converted into diphenylglycerol (m. p. 80—81°).

Phenyl glycidol ether,  $OPh\cdot CH_2\cdot CH{<}\begin{matrix}CH_2\\ |\\ O\end{matrix}$, boils at 234° with slight decomposition, but distils unchanged at 220° under a pressure of 520 mm.

Phenylglycerol, $OPh\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, is formed when the preceding compound is heated with water at 110—120°; it is a colourless, crystalline compound.

Paracresyl glycidol ether, $C_6H_4Me\cdot O\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ | \\ O\end{matrix}$, separates as an oil when epichlorohydrin is added to an alkaline solution of paracresol; it boils at 210° under a pressure of 200 mm. with slight decomposition.

Diparacresylglycerol, $OH\cdot CH(CH_2\cdot O\cdot C_6H_4Me)_2$, prepared by boiling paracresol with sodium ethoxide and epichlorohydrin in alcoholic solution, separates from alcohol and ether in colourless crystals and melts at 88°.

α-Naphthyl glycidol ether, $C_{10}H_7\cdot O\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ | \\ O\end{matrix}$, boils at about 263° with slight decomposition under a pressure of 200 mm.

Diglycidylcatechol, $C_6H_4(O\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ | \\ O\end{matrix})_2$, obtained by heating an alkaline solution of catechol with epichlorohydrin at 120°, separates from ether in lustrous, waxy crystals, melts at 83—84°, and is readily soluble in alcohol and ether, but only sparingly in hot water.

F. S. K.

Action of Formaldehyde on Phenols. By W. KLEEBERG (*Annalen*, **263**, 283—286).—Formaldehyde combines readily with phenol, resorcinol, and catechol, in presence of hydrochloric acid, but the products are insoluble in alkalis, and so difficult to purify that their composition could not be determined.

An *acid* of the composition $C_{16}H_{12}O_{10}$ is formed when concentrated hydrochloric acid is added to a warm aqueous solution of gallic acid and formaldehyde, and, on cooling, the product is deposited in an amorphous condition. It is purified by converting it into the *phenylhydrazine* salt, which crystallises in needles and has the composition $C_8H_6O_5,N_2H_3Ph$; on treating this salt with dilute hydrochloric acid, the acid is deposited in the form of a colourless, amorphous precipitate, which becomes crystalline when boiled for a long time with alcohol; the acid decomposes on heating, but without melting, and is only very sparingly soluble in alcohol, acetone, ether, benzene, and glacial acetic acid. The acid *ammonium* salt, $C_{16}H_{11}O_{10}\cdot NH_4$, is a reddish, crystalline compound.

F. S. K.

Orientation by Conversion of Paradinitro-derivatives into Quinones. By A. CLAUS, G. RAPS, E. HERFELDT, and W. BERKEFELD (*J. pr. Chem.* [2], **43**, 563—586).—The following compounds were investigated with a view to ascertaining whether the method employed by Claus and Runschke (Abstr., 1890, 1246) for the orientation of 4 : 6-dichlorometaxylene can be applied as a general method; the results obtained show that it can be so applied.

3 : 6-*Diamido*-2 : 5-*dibromoparisocymene* is obtained, contrary to Hömberg's statement (*J. pr. Chem.* [2], **42**, 114), when the corresponding dinitro-derivative is reduced by the usual means, but the reaction takes place with difficulty; if stannous chloride be used,

sufficient alcohol must be present to keep the dinitro-derivative in solution; if zinc or iron dust be used, the temperature must not be too high. In either case, the dried product is made alkaline, if necessary, and extracted with ether; the ethereal solution is treated with hydrogen chloride, whereby the *hydrochloride* is precipitated. The diamido-derivative crystallises in small, colourless needles, dissolves easily in ether and in alcohol, and melts at 105° (uncorr.). The *platinochloride* is described.

2 : 5-*Dibromoparisocymo*-3 : 6-*quinone* is formed when the aqueous solution of the hydrochloride of the diamido-derivative is oxidised by chromic acid, and separates from the liquid product in bright-yellow leaflets; it crystallises from alcohol in thick, yellow prisms, sublimes in feathery crystals, and melts at 74° (uncorr.). By reduction with aqueous sulphurous acid in a sealed tube at 100°, it yields the corresponding *quinol* [$Me : Pr^{\beta} : Br_2 : (OH)_2 = 1 : 4 : 2 : 5 : 3 : 6$]; this forms white crystals and melts at 64° (uncorr.).

Detailed directions are here given for obtaining a good yield (67 per cent. of theory) of metacymene by the method of Claus and Stüsser (Abstr., 1880, 632).

4 : 6-*Dibromometacymene*, obtained by the action of bromine (2 mols.) on metacymene in the presence of iron filings at the ordinary temperature, is a heavy, colourless, refractive, oily liquid; it boils at 281—283° (uncorr.), and is still liquid at −20°.

2 : 5-*Dinitro*-4 : 6-*dibromometacymene* is obtained by nitrating the dibromometacymene (1 part) with a well-cooled mixture (15 parts) of sulphuric acid (2 parts) and fuming nitric acid (1 part); the product is poured into ice-cold water and the precipitate crystallised, first from alcohol and finally from light petroleum. It forms long, slender, colourless needles, melts at 140—141° (uncorr.), sublimes, and dissolves fairly easily in the usual organic solvents. By reduction, it yields 2 : 5-*diamido*-4 : 6-*dibromometacymene*, which crystallises in small, colourless needles, melts at 95° (uncorr.), sublimes, and dissolves in most organic solvents, but not in water; its *hydrochloride* and *platinochloride* are described.

4 : 6-*Dibromometacymo*-2 : 5-*quinone*, produced by the oxidation of the diamido-derivative in acid solution, is best obtained pure by reducing the impure quinone, which is extracted from the product by ether, to the corresponding quinol (see below), purifying this by distillation with steam, and reoxidising it with chromic acid. The quinone is at first a waxy, buttery, yellow mass, but on prolonged exposure in a desiccator, at a low temperature, it crystallises in yellow needles; it melts at 32° (uncorr.), and is insoluble in cold water, little soluble in hot water, but freely in organic solvents; it will not sublime. 4 : 6-*Dibromometacymo*-2 : 5-*quinol* crystallises in slender, colourless needles, and melts at 153—154° (uncorr.); it distils with steam and sublimes in microscopic needles.

4 : 5-*Dibromorthocymene*, obtained by the action of bromine on orthocymene in presence of iron, is a colourless, oily liquid of agreeable, aromatic odour. 3 : 6-*Dinitro*- 4 : 5-*dibromorthocymene* forms small, colourless needles which melt at 148° (uncorr.), and are insoluble in water, very little soluble in cold but soluble in hot alcohol; it is

stable towards alkalis and can be heated with aniline without change. The corresponding *diamido*-derivative forms small needles, melts at 126° (uncorr.), and sublimes; in air and light it is unstable when moist, especially if impure; its *hydrochloride*, *platinochloride*, and *stannochloride* are described.

4 : 5-*Dibromorthocymo*-3 : 6-*quinone*, obtained from the diamido-derivative in the same way as the 2 : 5-quinone, is left on the evaporation of its ethereal solution as a yellow oil, which crystallises on cooling, and melts at 40° (uncorr.) ; it will not sublime. The corresponding *quinol* forms small, white needles, melts at 131° (uncorr.), and dissolves in hot water and the usual organic solvents; it is volatile with steam and sublimes; it is not oxidised to the quinone by chromic acid in the cold, a property which it shares with most other quinols which are halogenated in the benzene nucleus.

2 : 5-*Dibromoparacymene* is a heavy, colourless, refractive oil and boils at 283—284° (uncorr.), which is 10° higher than the boiling point of the corresponding derivative of parisocymene; when nitrated, it yields no oxidation products (compare Abstr., 1888, 583), the chief product being 3 : 6-*dinitro*-2 : 5-*dibromoparacymene*, which crystallises in colourless, vitreous needles melting at 156—157° (uncorr.). The corresponding *diamido*-derivative forms small, white needles which melt at 120—121° (uncorr.).

2 : 5-*Dibromoparacymo*-3 : 6-*quinone*, obtained by the oxidation of the last-mentioned diamido-derivative, crystallises in intensely yellow needles, melts at 30° (uncorr.), and is more stable and less deliquescent than the isomeric meta- and ortho-derivatives. The *quinol* forms small, colourless needles and melts at 138—139° (uncorr.).

The above results, obtained with the three synthetic (normal propyl) cymenes are in accord with the difference shown by Widmann (this vol., p. 687) to exist between synthetic paracymene and that obtained from camphor.

3 : 6-*Dinitro*-4 : 5-*dichlorortho-xylene* is obtained by nitrating dichlorortho-xylene (b. p. 227°, 1 part) in the cold with sulphuric acid (4 parts) and fuming nitric acid of sp. gr. 1·52 (5 parts) and then heating to boiling. It crystallises in colourless, transparent needles, melts at 155° (uncorr.), sublimes, and dissolves in alcohol. The corresponding *diamido*-derivative is best obtained when a dilute alcoholic solution of the dinitro-derivative is reduced with stannous chloride in presence of concentrated hydrochloric acid, and is purified by sublimation; it forms slender, white needles in feathery aggregates, melts at 176° (uncorr.), and is unstable in light and air when moist, especially, if impure. When ammonium sulphide acts on the dinitro-derivative, 3-*nitro*-6-*amido*-4 : 5-*dichlorortho-xylene* is formed; it crystallises in yellow needles, volatilises with steam, and melts at 54° (uncorr.).

4 : 5-*Dichlorortho-xylo*-3 : 6-*quinone* is formed when the diamido-derivative is oxidised with chromic acid; it crystallises in thin, yellow, lustrous leaflets, melts at 159° (uncorr.), sublimes, and dissolves very easily in alcohol, from which it will not crystallise. The corresponding *quinol* can only be obtained by heating the quinone with concentrated aqueous sulphurous acid in a sealed tube at 100°; it

crystallises in long, brilliant, lustrous, transparent, colourless needles, melts at 163—164° (uncorr.), sublimes, and dissolves in most organic solvents; its oxidation to the quinone by aqueous chromic acid is difficult. A. G. B.

Action of Sulphur Chloride on Aniline. By L. EDELEANO (*Bull. Soc. Chim.* [3], **5**, 173—175).—Sulphur chloride (20 grams) is added in drops to a solution of aniline (53 grams) in chloroform (500 c.c.), the temperature of the mixture being kept below 50° throughout the reaction. The aniline chloride formed in the reaction is filtered off, and spontaneous evaporation of the chloroform filtrate leaves a residue consisting of sulphur and of a portion which is soluble in hydrochloric acid. From the acid solution, alkalis precipitate a base, $S(C_6H_4{\cdot}NH_2)_2$, which crystallises from water in small, colourless, rectangular crystals melting at 107°. When sulphur chloride reacts on aniline dissolved in carbon bisulphide, a precipitate is formed of aniline hydrochloride and of diphenylthiocarbamide. No thioaniline is formed. T. G. N.

Methylparatoluidine. By E. BAMBERGER and P. WULZ (*Ber.*, **24**, 2077—2086).—In the course of their researches on the properties of tetrahydroquinolines (this vol., p. 1255), the authors have observed that when paradiazobenzenesulphonic acid acts on tetrahydro-3-methylquinoline, a mixture of an azo-colouring matter and the isomeric diazoamido-compound is formed even in presence of an excess of mineral acid. This reaction is so remarkable that the authors have also examined the action of paradiazobenzenesulphonic acid on methylparatoluidine, the "monocyclic" analogue of tetrahydro-3-methylquinoline, and find that the reaction proceeds in exactly the same manner in both cases.

To prepare methylparatoluidine, glacial formic acid and paratoluidine were heated together, the excess of the former distilled off in a vacuum, and the residue, which consists of *formoparatoluidide*, $C_6H_4Me{\cdot}NH{\cdot}CHO$, recrystallised from ether. It forms large, colourless prisms, melts at 53°, and on treatment with methyl iodide, potash, and a little alcohol, yields *methylformoparatoluidide*,

$$C_6H_4Me{\cdot}NMe{\cdot}CHO,$$

which distils at 273—277°, the distillate solidifying to large, brittle prisms. These melt at 30°, and are converted by fuming hydrochloric acid at 100° into *methylparatoluidine*, $C_6H_4Me{\cdot}NHMe$, which distils at 207—209° under a pressure of 715 mm. The *hydrochloride*, obtained by passing hydrogen chloride into the ethereal solution of the base, forms large, vitreous prisms, is readily soluble in water and alcohol, and melts at 119·5°. Its aqueous solution gives a reddish-brown coloration with ferric chloride, and becomes chestnut-brown on the addition of potassium dichromate and dilute sulphuric acid. The *nitroso*-compound, $C_6H_4Me{\cdot}NMe{\cdot}NO$, is readily obtained by the action of nitrous acid, and crystallises from ether in brownish-yellow, lustrous tablets, melts at 52—53°, and is reconverted into methylparatoluidine by the action of tin and hydrochloric acid. In this manner the methylated compound may readily be separated from any unaltered toluidine still present.

By the action of diazobenzenesulphonic acid, methylparatoluidine is, as already stated, converted into a mixture of an azo colour and the isomeric diazoamido-compound. The first compound, *methylparatoluidineorthoazobenzenesulphonic acid*, $NHMe{\cdot}C_6H_3Me{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$, crystallises in violet needles having a metallic lustre, and dissolves readily in boiling water with a dark raspberry-red colour, and also in alcohol, acetic acid, and concentrated sulphuric acid. It melts at 198—199°, and, in an acid bath, colours wool or silk dark orange. The *sodium* salt separates from an alkaline solution on the addition of sodium chloride in deep-red, crystalline flakes, which, on remaining under water, change to small, iridescent plates.

By the action of tin and hydrochloric acid, it is reduced to *orthamidomethylparatoluidine*, $NH_2{\cdot}C_6H_3Me{\cdot}NHMe$, which is extracted from the solution by ether after addition of soda. Hydrogen chloride is passed into the ethereal solution, and the precipitated reddish flakes at once dissolved in alcohol, as otherwise oxidation rapidly takes place. The *hydrochloride*, after recrystallisation, forms colourless, vitreous prisms, begins to melt at 175°, and decomposes at 180—185°. The free base crystallises from ether in colourless, prismatic tablets, melts at 43°, and is identical with the reduction product of nitromethylparatoluidine described by Gattermann (Abstr., 1875, 975). Like all orthodiamido-compounds, it gives a deep-red coloration with oxidising agents in acid solution, and, on boiling with acetic acid and sodium acetate, yields the *anhydro-base* or *imidazole*, $C_6H_3Me{<}\begin{smallmatrix}NMe\\ N\end{smallmatrix}{>}CMe$, which forms lustrous needles melting at 141·5—142°, and is identical with the compound obtained by Niementowski by the reduction of methylnitroparacetotoluidide.

Sulphobenzenediazoamidomethylparatoluidine,

$$NMe{\cdot}C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H,$$

is contained in the filtrate from the azo-compound. It is isolated as the *sodium* salt, which is a pure white substance sparingly soluble in water. With resorcinol and α-naphthylamine, it gives the colour reactions characteristic of diazoamido-compounds, and, on boiling with acids, yields nitrogen, phenolsulphonic acid, and methyltoluidine. The neutral aqueous solution gradually assumes a reddish colour, but the reaction is retarded by mineral acids. The *silver* salt, $C_{14}H_{14}N_3{\cdot}SO_3Ag$, forms white, lustrous needles, and decomposes on warming, with separation of silver; the majority of the other salts are sparingly soluble in water and crystallise well. H. G. C.

Adjacent Orthoxylidine. By K. Menton (*Annalen*, **263**, 316—339).—*Acetylmethylorthoxylidine*,

$$C_6H_3Me_2{\cdot}NMeAc\ [Me_2 : NMeAc = 1 : 2 : 3],$$

can be prepared by heating a xylene solution of acetylxylidine at 140° for 2—3 hours with a slight excess of the theoretical quantity of sodium, and carefully warming the sodium compound obtained in this way with methyl iodide; the product is extracted from the xylene solution with concentrated hydrochloric acid, the acid solution mixed with soda, and the precipitated base extracted with ether. It separates from hot light petroleum in well-defined crystals, melts at 75°, is only sparingly soluble in hot water, and is volatile with steam. It is not acted on by concentrated hydrochloric acid at 130°, or by boiling alcoholic potash, but when boiled with sulphuric acid (1 : 1·5) for 15 hours it is partially decomposed into methylorthoxylidine and acetic acid. The *platinochloride*, $(C_{11}H_{15}NO)_2,H_2PtCl_6$, crystallises from hot water in yellow needles. The *aurochloride* is precipitated in yellow crystals on adding auric chloride to a solution of the hydrochloride of the base; it has the composition

$$(C_{11}H_{15}NO)_2,HAuCl_4.$$

Methylorthoxylidine, $C_6H_3Me_2{\cdot}NHMe$, prepared by hydrolysing the acetyl derivative in the manner stated above, and purified by means of its nitroso-compound, is a pale-yellow oil boiling at 222—223°. The *hydrochloride*, $C_9H_{13}N,HCl$, crystallises in colourless needles; the acid *sulphate*, $C_9H_{13}N,H_2SO_4$, and the *platinochloride*,

$$(C_9H_{13}N)_2,H_2PtCl_6,$$

were also prepared. When the hydrochloride of the base is treated with sodium nitrite in ice-cold aqueous solution, the nitrosamine is precipitated as an oil, which, on treatment with alcoholic hydrochloric acid, undergoes intramolecular change, being converted into *paranitrosomethylorthoxylidine hydrochloride*, $NO{\cdot}C_6H_2Me_2{\cdot}NHMe,HCl$. The free *base*, obtained by decomposing this salt with sodium carbonate, crystallises from hot dilute alcohol in green needles, melts at 160—161°, and is only sparingly soluble in water, but readily in alcohol and benzene; when heated with aniline and aniline hydrochloride, it yields a red induline, as has been already stated by Fischer and Hepp (Abstr., 1890, 913), but owing to the difficulties experienced in hydrolysing acetylmethylorthoxylidine, a quantity of the nitroso-base sufficient for a thorough investigation of the induline could not be obtained.

Ethylorthoxylidine, $C_6H_3Me_2{\cdot}NHEt$ [$Me_2 : NHEt = 1 : 2 : 3$], is obtained when ethylacetylorthoxylidine, prepared from acetylorthoxylidine as described in the case of the corresponding methyl derivative, is heated with sulphuric acid (1 : 4) at 150—160° for several hours, but a considerable quantity of the acetyl derivative remains unchanged; when purified by means of its nitroso-derivative, it is obtained as an oil boiling at 227—228°. The *hydrochloride*,

$$C_{10}H_{15}N,HCl,$$

separates from alcoholic ether in crystals; the *platinochloride*,

$$(C_{10}H_{15}N)_2,H_2PtCl_6,$$

was also prepared. The *acetyl* derivative, $C_6H_3Me_2{\cdot}NEtAc$, is a yellow oil.

Paranitrosoethylorthoxylidine hydrochloride, $NO{\cdot}C_6H_2Me_2{\cdot}NHEt,HCl$, prepared by treating the nitrosamine with alcoholic hydrochloric acid, crystallises in slender, yellow needles; the free *base* crystallises from dilute alcohol in green needles and melts at 123—124°.

Trimethylxylidine ammonium iodide, $C_6H_3Me_2\cdot NMe_3I$, is formed, together with dimethylorthoxylidine, when orthoxylidine hydrochloride is heated at 180—190° for 10 hours with the theoretical quantity of methyl alcohol, and the mixture of methyl- and dimethyl-orthoxylidine obtained in this way boiled for 2—3 hours with methyl iodide; the product is treated with soda, and the dimethylorthoxylidine distilled with steam. The ammonium iodide separates from hot water in colourless crystals, decomposes on heating with liberation of methyl iodide, but without melting, and is readily soluble in water and alcohol.

Dimethylorthoxylidine, $C_6H_3Me_2\cdot NMe_2$, is an oil boiling at 199—200°. The *hydrochloride*, $C_{10}H_{15}N,HCl$, crystallises from alcoholic ether in slender needles, and is very readily soluble in water and alcohol. The *platinochloride*, $(C_{10}H_{15}N)_2,H_2PtCl_6$, separates from hot water in well-defined needles. A paranitroso-derivative of this base could not be obtained.

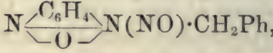
Benzeneazo-orthoxylidine hydrochloride, $NH_2\cdot C_6H_3Me_2\cdot N_2Ph,HCl$, is deposited in violet crystals when an aqueous solution of diazobenzene chloride is added, drop by drop, to an alcoholic solution of orthoxylidine heated at 40—45°; it is only sparingly soluble in alcohol and water. The free *base*, $C_{14}H_{15}N_3$, separates from a mixture of benzene and light petroleum in well-defined, reddish-yellow crystals melting at 98°.

Two bases are formed when paranitrosoethylorthoxylidine hydrochloride (see above) is heated with aniline and aniline hydrochloride at 130° for several hours, but they could not be obtained in a state of purity; they are both moderately easily soluble in alcohol yielding red solutions, but they have only feeble tinctorial properties.

Dimethylsafranine hydrochloride, $C_{20}H_{18}N_4,HCl$, is obtained, together with resinous products, when benzeneazo-orthoxylidine hydrochloride is heated with aniline at about 150°; it is precipitated from its aqueous solution, on the addition of sodium chloride, in the form of a red powder. It separates from alcohol in crystals, and dissolves in water with a beautiful red coloration; its alcoholic solution shows a brownish-yellow fluorescence. F. S. K.

Paranitrosobenzylaniline and Paranitrosobenzyltoluidine. By W. Boeddinghaus (*Annalen*, **263**, 300—313).—*Paranitrosobenzylaniline*, $C_{13}H_{12}N_2O$, can be obtained by heating an alcoholic solution of benzylaniline at 60° with amyl nitrite and a concentrated alcoholic solution of hydrogen chloride; when the reaction takes place in the cold, the principal product is benzylphenylnitrosamine. Paranitrosobenzylaniline crystallises from alcohol in beautiful green plates with a blue reflex, melts at 129°, and is readily soluble in benzene and hot alcohol, but only sparingly in cold alcohol and ether. The *hydrochloride*, $C_{13}H_{12}N_2O,HCl$, crystallises in slender, yellowish-brown needles, and is soluble in hot alcohol.

Benzylparaphenylenediamine, $NH_2\cdot C_6H_4\cdot NH\cdot CH_2Ph$, is formed when hydrogen sulphide is passed into an alcoholic ammoniacal solution of paranitrosobenzylaniline; it is purified by means of its *hydrochloride*, which crystallises from dilute alcohol in colourless, lustrous plates. The free base melts at 30°, and quickly turns red on exposure to the air.

Paranitrosophenylbenzylnitrosamine,  $\mathrm{N}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{O}\end{matrix}{>}\mathrm{N(NO){\cdot}CH_2Ph}$, is precipitated in yellowish needles when an aqueous solution of sodium nitrite is gradually added to a solution of paranitrosobenzylaniline sulphate with constant shaking; it melts at 77°, and is very unstable.

Paranitrosobenzylaniline combines with hydroxylamine hydrochloride in aqueous solution at the ordinary temperature, forming quinonedioxime and benzylamine hydrochloride; when boiled with dilute (1 : 20) soda, it yields paranitrosophenol, paramidophenol, benzaldehyde, and ammonia.

Paranitrosobenzylorthotoluidine, $C_{14}H_{14}N_2O$, can be obtained by treating benzylorthotoluidine with amyl nitrite and an alcoholic solution of hydrogen chloride as described above; it separates from hot alcohol in crystals, and melts at 115°. The *hydrochloride* is precipitated in crystals on passing hydrogen chloride into an ethereal solution of the base. When the base is boiled with dilute soda, it is completely decomposed, yielding benzaldehyde, ammonia, paranitroso- and paramido-orthocresol.

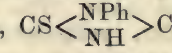
Benzylorthomethylparaphenylenediamine hydrochloride,

$$NH_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH_2Ph,2HCl,$$

is prepared by passing hydrogen sulphide into a warm, alcoholic ammoniacal solution of paranitrosobenzylorthotoluidine, evaporating the alcohol, dissolving the residual oil in ether, and adding an alcoholic solution of hydrogen chloride to the dried ethereal solution; it crystallises in slender, colourless needles. The free *base* melts at a low temperature, and is very unstable.

Paranitrosobenzylmetatoluidine, $C_{14}H_{14}N_2O$, prepared from benzylmetatoluidine as described in the case of the corresponding orthocompound, separates from alcohol in crystals, and melts at 121°.

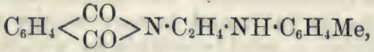
Paranitrosobenzylmethylaniline, $C_{14}H_{14}N_2O$, is obtained when an alcoholic solution of benzylmethylaniline is heated with amyl nitrite and an alcoholic solution of hydrogen chloride at 60°, and the salt thus produced decomposed with ammonia; it separates from alcohol in crystals, melts at 56°, and is decomposed by boiling soda yielding, as principal product, benzylmethylaniline, and small quantities of benzaldehyde and methylamine. F. S. K.

Derivatives of Ethylenephenyldiamine and its Homologues. By H. E. NEWMAN (*Ber.*, **24**, 2191—2200).—*Ethylenephenylthiocarbamide*,  $\mathrm{CS}{<}\begin{matrix}\mathrm{NPh}\\ \mathrm{NH}\end{matrix}{>}\mathrm{C_2H_4}$, is obtained when ethylenephenyldiamine (compare Gabriel, Abstr., 1889, 1166) is treated with carbon bisulphide, and the yellow, crystalline product heated with water; it is also formed in small quantities when potassium thiocarbimide is heated at

140° with ethylenephenyldiamine hydrochloride. It separates from hot water in colourless, lustrous crystals, melts at 155°, and is readily soluble in alcohol and benzene, but only sparingly in carbon bisulphide and ether, and insoluble in light petroleum and cold hydrochloric acid.

Ethylenephenylcarbamide, $C_9H_{10}N_2O$, can be prepared by heating ethylenephenyldiamine hydrochloride with potassium cyanate at 130°; it crystallises from hot water in almost colourless plates, melts at 160—161°, and is readily soluble in benzene and alcohol, but only sparingly in ether and carbon bisulphide, and insoluble in cold water and light petroleum.

Dibenzoylethylenephenyldiamine, $C_{22}H_{20}N_2O_2$, prepared by shaking the diamine with benzoic chloride and potash, crystallises from alcohol in colourless prisms, melts at 143·5°, and is soluble in benzene and ether, but insoluble in water and light petroleum; it distils without decomposition, and has feeble basic properties. The corresponding *acetyl* derivative, $C_{12}H_{16}N_2O_2$, separates from hot benzene in colourless, rhombic crystals, melts at 116°, and is very readily soluble in water and alcohol, but more sparingly in ether and toluene, and insoluble in light petroleum; it forms a crystalline acetate, which is readily soluble in water and alcohol, and, when heated in a stream of hydrogen chloride, it is converted into an anhydro-base, the *platinochloride* of which has the composition $C_{20}H_{24}N_4,H_2PtCl_6$, and is readily soluble in water.

Orthotoluidoethylphthalimide,  $C_6H_4<{}^{CO}_{CO}>N{\cdot}C_2H_4{\cdot}NH{\cdot}C_6H_4Me$, is easily obtained by heating bromethylphthalimide with orthotoluidine at 130°; it crystallises from boiling alcohol in short, yellowish needles, melts at 153°, and is readily soluble in ether and carbon bisulphide, but only sparingly in cold water and light petroleum, and insoluble in water.

Ethyleneorthotolyldiamine, $NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}C_6H_4Me$, is obtained when the preceding compound is boiled with concentrated hydrochloric acid for three hours, and the hydrochloride produced in this way decomposed with soda; it is an oil, boils at about 267°, is soluble in water and alcohol, and absorbs carbonic anhydride from the air. The *hydrochloride* crystallises in plates, and melts at 168—173°. The *picrate*, $C_9H_{14}N_2,2C_6H_3N_3O_7$, crystallises in green needles, and melts at 148°. The *dibenzoyl* derivative, $C_9H_{12}N_2Bz_2$, forms prismatic needles, melts at 164·5°, and has feeble basic properties.

Paratoluidoethylphthalimide, $C_{17}H_{16}N_2O_2$, is formed, together with a compound melting at 200°, when bromethylphthalimide is heated with paratoluidine at 140°; the two compounds are separated by means of boiling alcohol. The imide separates from hot alcohol in yellow crystals, melts at 96°, and is very readily soluble in benzene, carbon bisulphide, and glacial acetic acid, but only sparingly in ether and cold alcohol, and insoluble in water and light petroleum. The compound melting at 200° separates from warm benzene in lemon-yellow crystals, and is readily soluble in glacial acetic acid, but only sparingly in ether and carbon bisulphide, and insoluble in water, light petroleum, and boiling alcohol; it is probably a diphthalyl derivative of diethyleneparatolyltetramine of the constitution $C_6H_4Me\cdot N(C_2H_4\cdot N\colon C_8H_4O_2)_2$.

Ethyleneparatolyldiamine hydrochloride, $C_9H_{14}N_2,2HCl$, prepared by heating paratoluidoethylphthalimide with concentrated hydrochloric acid, crystallises from hot alcohol in long, colourless needles, sinters together at 210°, and melts at 218°; the free *base*, $C_9H_{14}N_2$, is a colourless oil. The *platinochloride* crystallises in yellowish plates, and is only sparingly soluble in alcohol, but readily in water. The *dibenzoyl* derivative, $C_9H_{12}N_2Bz_2$, crystallises from alcohol in small, colourless needles, melts at 161°, and is readily soluble in alcohol and glacial acetic acid, but only sparingly in benzene, and almost insoluble in light petroleum, carbon bisulphide, and water. The *diacetyl* derivative, $C_9H_{12}N_2Ac_2$, separates from hot benzene in cubic crystals, melts at 107°, and is very readily soluble in water, alcohol, and glacial acetic acid, but insoluble in carbon bisulphide and light petroleum.

Metaxylidoethylphthalimide, $C_6H_3Me_2\cdot NH\cdot C_2H_4\cdot N\colon C_8H_4O_2$, crystallises from boiling alcohol in small needles, melts at 123°, and is very readily soluble in benzene, glacial acetic acid, and carbon bisulphide, but only sparingly in cold alcohol and ether.

Ethylenemetaxylyldiamine, $NH_2\cdot C_2H_4\cdot NH\cdot C_6H_3Me_2$, is a colourless oil which boils at 273—275°, and absorbs carbonic anhydride from the air. The *hydrochloride* is deliquescent, sinters together at 168°, and melts at 173°. The *picrate* crystallises in reddish-yellow needles, melts at 141°, and is very readily soluble in alcohol. The *platinochloride* is readily soluble in water, but almost insoluble in alcohol, and has the composition $C_{10}H_{16}N_2,HCl,PtCl_4$.

ψ-Cumidoethylphthalimide, $C_6H_2Me_3\cdot NH\cdot C_2H_4\cdot N\colon C_8H_4O_2$, crystallises from hot alcohol in orange needles, sinters together at 143°, and melts at 146°.

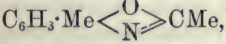
α-Naphthylamidoethylphthalimide, $C_{10}H_7\cdot NH\cdot C_2H_4\cdot N\colon C_8H_4O_2$, separates from boiling alcohol in yellow crystals, melts at 158°, and is readily soluble in benzene and glacial acetic acid, but only sparingly in ether; when heated with concentrated hydrochloric acid at 150—160°, it is decomposed into phthalic acid and *ethylene-α-naphthyldiamine*, the *picrate* of which crystallises in small, red needles, melts at 211°, and has the composition $C_{12}H_{14}N_2,C_6H_3N_3O_7$.

β-Naphthylamidoethylphthalimide, $C_{20}H_{16}N_2O_2$, crystallises from hot alcohol in almost colourless needles, melts at 141°, and is readily soluble in benzene, glacial acetic acid, and carbon bisulphide; it is not decomposed by hydrochloric acid.

Methylanilidoethylphthalimide, $NMePh\cdot C_2H_4\cdot N\colon C_8H_4O_2$, prepared by heating bromethylphthalimide with methylaniline at 160—170°, crystallises from alcohol in greenish-yellow, quadratic plates, melts at 104—105°, and is very readily soluble in benzene, carbon bisulphide, and hot alcohol, but only sparingly in ether and cold alcohol. It is readily decomposed by hydrochloric acid, yielding *ethylenemethylphenyldiamine hydrochloride*, $C_9H_{14}N_2,2HCl$; the free *base* is a colourless oil boiling at 254—255°, readily soluble in alcohol and water; the *picrate* crystallises in needles, sinters together at 165°, melts at 173°, and is readily soluble in alcohol, but only sparingly in water.

F. S. K.

Hydroxyazo-compounds. By H. GOLDSCHMIDT and R. BRUBACHER (*Ber.*, **24**, 2300—2317; see also Abstr., 1890, 614).—The paper is a continuation of the author's work on the constitution of hydroxyazo-compounds to determine if they are hydroxylated azo-compounds or hydrazones of quinones. The authors have examined the behaviour of the acetates and benzoates of these compounds on reduction; they find that the ethereal salts of the parahydroxy-compounds behave like the compounds obtained by the action of phenyl cyanate, but the ortho-compounds in some cases are split up into their constituents, so that the position of the acid residue can be determined.

Orthohydroxyazo-compounds.—Acetylbenzeneazoparacresol is prepared by heating benzeneazoparacresol with acetic anhydride, and melts at 87—88°. The reduction is carried out as follows:—The acetate is dissolved in cold alcohol, zinc-dust added, and then dilute acetic acid; the solution becomes colourless. It is filtered, acidified with hydrochloric acid, and extracted with ether. The ethereal solution contains acetanilide, and the aqueous solution amidoparacresol [$Me : NH_2 : OH = 1 : 3 : 4$]. The authors maintain that this reaction is not to be explained by the usual formula of the azo-compound, $Ph{\cdot}N_2{\cdot}C_6H_3Me{\cdot}OAc$, which would be expected to yield aniline and ethenylamidocresol,  $C_6H_3{\cdot}Me{<}\genfrac{}{}{0pt}{}{O}{N}{>}CMe$, or amidocresol and acetic acid. He explains the reaction by giving the azo-compound the formula $O{:}C_6H_3Me{:}N{\cdot}NPhAc$, and then benzeneazoparacresol is represented as the phenylhydrazone of orthotoluquinone. The same products of reduction were obtained by employing zinc-dust and formic acid in place of acetic acid.

Acetylbenzenehydrazoparacresol, $OH{\cdot}C_6H_3Me{\cdot}NH{\cdot}NPhAc$, is obtained by reducing the above azo-compound dissolved in alcohol and acetic acid with sodium amalgam (2·5 per cent.) in an atmosphere of carbonic anhydride. On adding water, the compound is precipitated in white, microscopic leaflets; it melts at 124—125°, is very unstable, and decomposes on recrystallisation. It dissolves at once in sodium hydroxide to a reddish-yellow solution, with decomposition, and on reduction with zinc-dust and acetic acid yields amidocresol and acetanilide.

Benzoylbenzeneazoparacresol is obtained from benzeneazocresol by the action of benzoic chloride or benzoic anhydride. When reduced with zinc-dust and acetic acid, it yields *benzoylbenzenehydrazoparacresol*. The latter crystallises from benzene on the addition of light petroleum in white needles, and melts at 152°. When treated with alkali, it remains undissolved at first, but soon goes into solution with decomposition.

Acetylbenzeneazo-β-naphthol and benzoylbenzeneazo-β-naphthol, when reduced with zinc-dust and acetic acid, yield amido-β-naphthol, and acetanilide and benzanilide respectively.

Acetylbenzeneazopseudocuminol crystallises from alcohol in reddish-yellow needles, and melts at 73—74°. When reduced in cold alcoholic solution with zinc-dust and acetic acid, *acetylbenzenehydrazopseudocuminol* is obtained. The latter crystallises from benzene and light petroleum in white leaflets, and melts at 123°. When a large quantity of acetic acid is employed, and the reduction allowed to take place without cooling, the azo-compound is split into amidopseudocuminol and acetanilide.

The authors were unable to prepare the benzoyl derivative of benzeneazopseudocuminol.

Orthonitrobenzeneazoparacresol is obtained by the action of orthonitrodiazobenzene chloride on an alkaline solution of paracresol. It crystallises from alcohol in red needles, and melts at 118°. The *acetyl* derivative, obtained by boiling it with acetic anhydride, crystallises from alcohol in yellow, prismatic needles, and melts at 99—100°. The product obtained from it on reduction with zinc-dust and acetic acid could not be obtained crystalline, and lack of material prevented further experiments.

Parahydroxyazo-compounds.—The acetyl and benzoyl derivatives of parahydroxyazo-compounds, on reduction with zinc-dust and acetic acid, give only the corresponding hydrazo-compounds. These are insoluble in alkalis, which seems not to be conformable with the hydrazone formula. However, acetylparatolueneazophenol yields a phenolic compound belonging to the diphenyl series, and hence does not behave in accordance with the hydroxyazo-formula.

Acetylhydroxyazobenzene, when reduced as described above with zinc-dust and acetic acid, yields *acetylhydroxyhydrazobenzene.* The latter is obtained in white needles by precipitation from benzene with light petroleum, melts at 114—115°, and is easily soluble in alcohol and benzene, sparingly in light petroleum.

Benzoylhydroxyhydrazobenzene is obtained in a similar way by reduction of benzoylhydroxyazobenzene; it crystallises in white prisms, melts at 173°, and is easily soluble in alcohol, benzene, and ether.

Acetylparatolueneazophenol, obtained by boiling tolueneazophenol with acetic anhydride, crystallises from alcohol in orange-yellow needles, and melts at 95°. On reduction with zinc-dust and acetic acid, it yields the corresponding *hydrazo-compound*, which crystallises from benzene and petroleum in white prisms, and melts at 106°. The azo-compound is more difficult to reduce with zinc-dust and sulphuric acid, and the mixture requires heating on the water-bath for some time. When the reduction is complete, the mixture is made alkaline, and extracted with ether. The ethereal extract contains paratoluidine. The alkaline solution rapidly becomes blue; it was acidified and again extracted with ether, when a compound was obtained isomeric with the above hydrazo-compound; this melts at 141°, is soluble in acids and strong sodium hydroxide, and becomes intensely blue in alkaline solution on exposure. Ferric chloride colours the acid solution dark-red. The author believes it to be a diphenyl derivative of the constitution [$OH : NH_2 : Me : NHAc = 3 : 6 : 3' : 6'$].

Pseudocumeneazophenol is prepared by the action of diazopseudocumene chloride on phenol dissolved in soda. It is precipitated from the solution by carbonic anhydride, and may be purified by dissolving it in strong ammonia and reprecipitation, it forms small, yellow leaflets, melts at 94°, and is easily soluble in alcohol and benzene, sparingly in light petroleum. The *acetyl* compound, prepared by boiling it with acetic anhydride, crystallises from alcohol in long, orange-red needles, and melts at 105°.

Acetylpseudocumenehydrazophenol is obtained by reducing the foregoing compound with zinc-dust and acetic acid; it crystallises from benzene and petroleum in long, colourless needles, and melts at 102—103°.

The acetate and benzoate of benzeneazo-α-naphthol yield the corresponding hydrazo-compounds on reduction.

Acetylbenzenehydrazo-α-naphthol crystallises from benzene and petroleum in white leaflets, and melts at 157°.

Benzoylbenzenehydrazo-α-naphthol crystallises in small prisms, melts at 162°, and is easily soluble in alcohol, ether, and benzene.

Acetylorthonitrohydroxyazobenzene, obtained by heating the azo-compound with acetic anhydride, separates from alcohol in yellow crystals, and melts at 109°. On reduction with zinc-dust and acetic acid, it yielded products which were difficult to obtain crystalline. On reduction with zinc and hydrochloric acid, orthophenylenediamine was obtained.

The authors formulate all the above compounds as hydrazones of quinones, and maintain that the results are in agreement with these formulæ. They also discuss the two most powerful arguments in favour of the old formulæ, namely, the behaviour of hydroxyazo-compounds on alkylation, and their formation from diazo-salts and phenols, and show that they do not necessarily compel the acceptance of the old formula. E. C. R.

Cryoscopic Experiments. By H. GOLDSCHMIDT (*Ber.*, **24**, 2317—2323).—Diazoamido-compounds dissolved in aromatic amines very easily undergo change into amidoazo-compounds in the presence of salts of aromatic amines. The author has instituted a series of experiments to determine if the hydrochlorides of aniline bases which are electrolytes in aqueous solution are also capable of dissociation when dissolved in amines. The method employed was to observe the lowering of the freezing point of the solution. Paratoluidine was employed as the solvent (Eykman, *Zeit. physikal. Chem.*, **4**, 497). Diazoamido-compounds, amidoazo-compounds, aromatic amines, and their salts were examined. The results show that the electrolytes do not give a larger molecular depression than the non-electrolytes. The non-electrolytes give numbers agreeing with Eykman's; the electrolytes give numbers distinctly lower.

The molecular depressions of diazoamido-compounds, amidoazo-compounds, and aromatic amines are near together, and are near to the number determined by Eykman for many compounds, that is, about 51. Aniline gives a smaller constant than β-naphthylamine.

Paratoluidine hydrochloride, benzylamine hydrochloride, and trimethylphenylium iodide give a molecular depression of about 40. Aniline, pseudocumidine, and β-naphthylamine hydrochlorides give very large molecular depressions, the explanation being that in solution in paratoluidine these salts are decomposed with formation of the free base and paratoluidine hydrochloride. The observed molecular depressions were about equal to the sum of the depressions of the free base and paratoluidine hydrochloride.

The author has studied the conversion of diazoamidobenzene into amidoazotoluene by paratoluidine hydrochloride in paratoluidine solution. On adding paratoluidine hydrochloride to the solution of the diazoamido-compound, a lowering of the freezing point was observed, corresponding with the evolution of 2 mols. of aniline, as expressed in the equation

$$PhN_2{\cdot}NHPh + 2C_7H_7{\cdot}NH_2 = C_7H_7{\cdot}N_2{\cdot}C_7H_6{\cdot}NH_2 + 2PhNH_2.$$

The author is engaged on the further study of these phenomena.

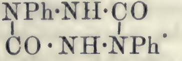
E. C. R.

Action of Carbonyl Sulphide, Carbonyl Chloride, and Alkyl Chlorocarbonates on Phenylhydrazine. By G. HELLER (*Annalen*, **263**, 269—283).—*Phenylhydrazine phenylsemithiocarbazate*, $C_{13}H_{16}N_4O$, is obtained in crystals when carbonyl sulphide is passed into a well-cooled, ethereal solution of phenylhydrazine; it melts at 82—84° with decomposition, when quickly heated, and is only sparingly soluble in water, benzene, ether, and light petroleum, but more readily in alcohol and chloroform. It is unstable, reduces Fehling's solution on boiling, and has, probably, the constitution $NHPh{\cdot}NH{\cdot}CO{\cdot}SH,NH_2{\cdot}NHPh$. When treated with warm alcoholic ammonia, it is converted into a crystalline compound of the composition $C_7H_{11}N_3OS$; this substance is readily soluble in water, warm alcohol, and acetone, but more sparingly in ether, chloroform, and benzene, and is probably the ammonium salt of the acid. In aqueous solutions of this ammonium salt, metallic salts produce precipitates which are decomposed on boiling, with formation of the sulphide of the metal; the free acid cannot be isolated. When phenylhydrazine phenylsemithiocarbazate is heated in open vessels at a temperature above its melting point, it is completely decomposed, leaving a residue of phenylhydrazine; but when the dry salt is heated in sealed tubes it is converted into diphenylcarbazide (m. p. 163°), carbamide, aniline, diphenylcarbamide, carbon bisulphide, and ammonia.

Diphenylcarbazone, $NPh{:}N{\cdot}CO{\cdot}NH{\cdot}NHPh$, is obtained when diphenylcarbazide is boiled for about 10 minutes with alcoholic potash, and the cold, filtered solution acidified with dilute sulphuric acid. It crystallises from benzene in orange-red needles, melts at 157° with decomposition, and is readily soluble in alcohol, benzene, and chloroform, but insoluble in water; it dissolves in cold, concentrated sulphuric acid, yielding an intensely carmine-red solution. Its alkaline solution reduces Fehling's solution, gives precipitates with solutions of metallic salts, and is readily reduced by alcohol and zinc-dust, with formation of diphenylcarbazide.

Phenylhydrazine and carbonyl chloride combine readily in ethereal solution, forming diphenylcarbazide, phenylhydrazine hydrochloride, and a small quantity of a compound of high melting point, the nature of which was not determined; under the same conditions, phenylhydrazine and thionyl chloride yield diphenylthiocarbazide and phenylhydrazine hydrochloride.

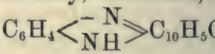
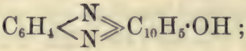
Ethyl phenylcarbazate, NHPh·NH·COOEt, is obtained when an ethereal solution of ethyl chlorocarbonate is gradually added to a well-cooled ethereal solution of phenylhydrazine, with constant shaking; it crystallises from hot water in yellowish needles, melts at 86—87°, and is only sparingly soluble in cold water, but readily in alcohol, acetone, benzene, chloroform, ether, and hot water. It reduces Fehling's solution on warming, dissolves freely in concentrated mineral acids, and, on oxidation with mercuric oxide in chloroform solution, it seems to be converted into an azo-compound of the constitution NPh:N·COOEt; when heated with aniline at 210—215° it is converted into diphenylsemicarbazide (m. p. 172—173°). The *acetyl* derivative, $C_{11}H_{14}N_2O_3$, crystallises from water in slender, colourless needles, sinters together at 97°, melts at 102—103°, and is only sparingly soluble in ether and light petroleum, but more readily in alcohol, benzene, acetone, chloroform, and glacial acetic acid.

Methyl phenylcarbazate, NHPh·NH·COOMe, prepared from methyl chlorocarbonate in like manner, crystallises from water in prisms, melts at 115—117°, and resembles the ethyl salt in properties. When heated at 230—240° for some time, it is decomposed into methyl alcohol and diphenylurazine (m. p. 264°), identical with the compound obtained by Pinner (*Ber.*, **21**, 2330) from phenylsemicarbazide; the constitution of diphenylurazine is most probably expressed by the formula  $\begin{array}{l} NPh\cdot NH\cdot CO \\ | \qquad\qquad\quad | \\ CO\cdot NH\cdot NPh \end{array}$. The ethyl salt undergoes an analogous decomposition into ethyl alcohol and diphenylurazine.

F. S. K.

Relations between Eurhodines, Indulines, and Safranines. By F. KEHRMANN and J. MESSINGER (*Ber.*, **24**, 2167—2175; compare this vol., p. 746).—*Methylrosindulone*, $C_{17}H_{12}N_2O$, is deposited in crystals when hydroxynaphthaquinone is treated with methylorthophenylenediamine in concentrated alcoholic solution; it crystallises from a mixture of alcohol and benzene in vermilion needles having a green reflex, melts at 257—259°, and is rather sparingly soluble in ether, alcohol, and benzene, yielding yellowish-red solutions which show a vermilion fluorescence. Its solution in concentrated sulphuric acid is dichroïc, being dirty green in thin, and dark purple-red in thick, layers; on diluting with water the solution turns orange-red. The hydrochloride crystallises in brown needles having a green reflex, and is decomposed by water. On adding bromine-water to an acid alcoholic solution of methylrosindulone, until the solution smells of the halogen after shaking, and then immediately adding excess of sulphurous acid, a *bromo*-derivative is precipitated in red crystals; it separates from glacial acetic acid in green needles, decomposes at about 250°, but without melting, is very sparingly soluble in most ordinary organic solvents, and dissolves in concentrated sulphuric acid with a dark-green coloration. The constitution of methylrosindulone is, doubtless, expressed by the formula $C_6H_4{<}\genfrac{}{}{0pt}{}{\overline{}N}{NMe}{>}C_{10}H_5O$.

Methoxynaphthaphenazine, $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}C_{10}H_5\cdot OMe$, is formed, together with methylrosindulone, when the eurhodole, prepared from hydroxynaphthaquinone and orthophenylenediamine as previously described, is boiled with methyl iodide and soda in methyl alcoholic solution. The two products are precipitated with water, the precipitate dissolved in boiling alcohol, the solution mixed with concentrated hydrochloric acid, and the methoxynaphthaphenazine carefully precipitated with water; on adding ammonia to the filtrate, methylrosindulone, identical with the compound just described, is precipitated. Methoxynaphthaphenazine crystallises from boiling alcohol in long, light-yellow needles, melts at 176—177°, and sublimes at a higher temperature. It is insoluble in alkalis, but moderately easily soluble in boiling alcohol, benzene, glacial acetic acid, &c., and it dissolves in concentrated sulphuric acid yielding an intensely yellow solution, from which a salt is precipitated in almost colourless needles on the addition of water; its solutions do not give a precipitate with bromine-water.

The above experiments prove that α-naphthaeurhodole exists in two tautomeric modifications, and its constitution may, therefore, be expressed both by the quinoneimide formula  $C_6H_4{<}\substack{-N\\NH}{>}C_{10}H_5O$ and by the hydroxy-formula  $C_6H_4{<}\substack{N\\N}{>}C_{10}H_5{\cdot}OH$; it is almost superfluous to remark that the constitution of eurhodoles and eurhodines can be expressed by the quinoneimide formula only when they contain a hydroxy- or amido-group in the para-, or perhaps also in the ortho-, position to one of the azine-nitrogen atoms; this is probably also true in the case of the safranines. F. S. K.

Benzylthiocarbimide. By V. Meyer (*Annalen*, **264**, 125—127).—An attempt to prepare an alkyl derivative of benzylthiocarbimide was unsuccessful; when benzylthiocarbimide is treated with benzyl chloride and sodium ethoxide in alcoholic solution, benzyl sulphide is formed.

Hydroxylamine is not very rapidly decomposed by boiling, concentrated soda, and the distillate obtained from such a mixture frequently contains considerable quantities of the nitrogenous base.

F. S. K.

Compounds prepared from Methylphenylchloroformamide and Diphenylchloroformamide. By E. Lellmann and E. Benz (*Ber.*, **24**, 2108—2116; see also Lellman and Barhöfer, Abstr., 1887, 935).—Methylphenylchloroformamide readily acts on potassium phenate in alcoholic solution, yielding potassium chloride and *phenyl methylphenylcarbamate*, $NPhMe{\cdot}COOPh$, which forms large, colourless crystals, melts at 58°, and is readily soluble in alcohol, ether, chloroform, and benzene. *Orthonitrophenyl methylphenylcarbamate*,

$$NPhMe{\cdot}COO{\cdot}C_6H_4{\cdot}NO_2,$$

is prepared in a similar manner from potassium orthonitrophenate, and crystallises in monosymmetric prisms

$$(a : b : c = 1{\cdot}34084 : 1 : 1{\cdot}09509,\ \beta = 100°\ 38').$$

It melts at 110°, and is sparingly soluble in cold, readily in hot, alcohol. The *paranitrophenyl* and *metanitrophenyl* salts are both crystalline compounds, and melt at 69—70° and 105° respectively.

Orthamidophenyl methylphenylcarbamate, $NPhMe\cdot COO\cdot C_6H_4\cdot NH_2$, is obtained by reducing the orthonitro-compound with stannous chloride and hydrochloric acid, and crystallises from alcohol in slender needles melting at 103°. The *paramido*-compound forms needles melting at 104°, and the *metamido*-compound is a yellow, crystalline powder melting at 94°. *Paracresyl methylphenylcarbamate*,

$$NPhMe\cdot COOC_6H_4Me,$$

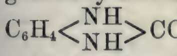
is prepared in the same way as the phenyl compound, and forms slender needles melting at 62°.

Paranitrophenyl diphenylcarbamate, $NPh_2\cdot COO\cdot C_6H_4\cdot NO_2$, crystallises in slender, pale-yellow needles, and melts at 116°, whilst the *metanitro*-compound forms nacreous plates, and melts at 90°. *Paramidophenyl diphenylcarbamate*, $NPh_2\cdot COO\cdot C_6H_4\cdot NH_2$, obtained by the reduction of the paranitro-compound, forms yellowish needles, and melts at 146°, whilst the *metamido*-compound crystallises in reddish needles, and melts at 132—133°. *Paracresyl diphenylcarbamate*, $NPh_2\cdot COO\cdot C_6H_4Me$, crystallises from alcohol in silky, asbestos-like aggregates of needles, and melts at 81°.

Methyldiphenylchloroformamide also combines with amido-bases; thus with aniline it yields methylcarbanilide at the ordinary temperature, but on warming gives diphenylcarbamide almost exclusively. *Methylphenylmetanitrophenylcarbamide*, $NPhMe\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2$, is readily obtained by the action of 2 mols. of metanitraniline on 1 mol. of methylphenylchloroformamide at 90°, and forms greenish-yellow needles which melt at 230°, and dissolve readily in hot alcohol. On reduction with stannous chloride and hydrochloric acid, it is converted into *methylphenylmetamidophenylcarbamide*,

$$NPhMe\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2,$$

which crystallises in white, matted needles, and, at 190—200°, gradually decomposes into methylaniline and metaphenylenecarbamide


$C_6H_4{<}^{NH}_{NH}{>}CO$ (compare Abstr., 1885, 977).

Methylphenylchloroformamide also reacts with aromatic hydrocarbons in presence of aluminium chloride. Benzene is thus converted into benzoylmethylanilide, and toluene into *methylphenylparatoluamide*, $C_6H_4Me\cdot CO\cdot NMePh$; the latter crystallises in large, yellowish, monosymmetric crystals ($a : b : c = 2\cdot67609 : 1 : 2\cdot35724$, $\beta = 108° 44'$), melts at 70°, is readily soluble in alcohol, ether, chloroform, and light petroleum, and, on hydrolysis, yields paratoluic acid and methylaniline. *Methylphenylxyloylamide*, $C_6H_3Me_2\cdot CO\cdot NMePh$ ($CH_3 : CH_3 : CO\cdot NMePh = 4 : 2 : 1$), is obtained in the same way from metaxylene, and crystallises from light petroleum in small, pale-yellow crystals melting at 54°. The corresponding 4 : 3 : 1-compound, prepared from orthoxylene, forms large, flesh-coloured, asymmetric crystals ($a : b : c = 0\cdot49009 : 1 : 0\cdot55605$, $\alpha = 118° 7' 20''$, $\beta = 109° 44' 40''$, $\gamma = 58° 83'$; $A = 111° 33' 50''$, $B = 97° 0' 50''$, $C =$

64° 6′ 20″), and melts at 78°; whilst the 5 : 2 : 1-compound from paraxylene crystallises from ether in pink plates, and melts at 74°. The last three compounds all yield the corresponding xylylic acids on hydrolysis. H. G. C.

Seleno- and Thio-derivatives of Ethylamine and Propylamine. By V. Coblentz (*Ber.*, **24**, 2131—2136): compare Gabriel and Lauer, Abstr., 1890, 472).—*Thiocarbimidoethylphthalimide*,

$$C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}SCN,$$

prepared by heating bromethylphthalimide with potassium thiocarbimide at 100° in alcoholic solution, separates from alcohol in colourless crystals melting at 108°; when treated with 10 per cent. potash, it is converted into *ethyldisulphidediphthalamic acid*,

$$S_2(CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH)_2.$$

This acid separates from hot alcohol in colourless crystals, melts at 128—130°, and is decomposed by concentrated hydrochloric acid at 180° into phthalic acid and dithioethylamine (compare Coblentz and Gabriel, this vol., p. 817); the *picrate* of this base crystallises from hot alcohol in yellow needles, melts at 198—200°, and has the composition $C_4H_{12}N_2S_2,2C_6H_3N_3O_7$.

β-Selenocarbimidoethylphthalimide, $C_8H_4O_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}SeCN$, obtained in like manner from potassium selenocyanide, is a colourless, crystalline compound melting at 124—125°; when boiled with 10 per cent. potash, it is converted into *ethyl-β-diselenidodiphthalamic acid*, $Se_2(CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH)_2$, a yellowish, crystalline compound melting at 118—119°.

γ-Selenocarbimidopropylphthalimide, $C_{12}H_{10}N_2SeO_2$, prepared from bromopropylphthalimide and potassium selenocyanide, melts at 102°, and is converted into *propyl-γ-diselenidodiphthalamic acid*,

$$C_{22}H_{24}N_2O_6Se_2,$$

by hot potash; this acid separates from alcohol in crystals melting at 84°.

Diselenoethylamine hydrochloride, $Se_2(CH_2{\cdot}CH_2{\cdot}NH_2)_2,2HCl$, is obtained when ethyl-β-diselenidodiphthalamic acid is heated at 180° with concentrated hydrochloric acid; it melts at 188°. The *picrate*, $C_4H_{12}N_2Se_2,2C_6H_3N_3O_7$, crystallises from alcohol in orange needles, and melts at 178°.

Diselenopropylamine hydrochloride, $C_6H_{16}N_2Se_2,2HCl$, prepared from propyl-γ-diselenidophthalamic acid in like manner, separates from alcohol in crystals melting at 170°; the *picrate*, $C_6H_{16}N_2Se_2,2C_6H_3N_3O_7$, forms orange crystals, and melts at 165°. F. S. K.

Action of Alkali Hypochlorites and Hypobromites on some Imides and Phthalodiamide. By S. Hoogewerff and W. A. van Dorp (*Rec. Trav. Chim.*, **10**, 4—12).—Succinimide, treated in alkaline solution with potassium hypobromite, yields β-amidopropionic acid.

The imide (1 mol.) is dissolved in a solution containing potash

(6 mols.) and hypobromite (1 mol.), and heated for two hours at 50—60°. The liquid contains potassium β-amidopropionate; it is acidified with hydrochloric acid, evaporated to dryness, mixed with absolute alcohol, and dry hydrogen chloride passed through the mixture, which is then filtered, and the filtrate evaporated to dryness. The residue is dissolved in water, and treated on the water-bath with silver sulphate, again filtered, traces of silver precipitated with hydrogen sulphide, and finally it is boiled with baryta in excess. The barium salt now in solution is decomposed by sulphuric acid, and the filtrate evaporated. The melting point found by the authors for β-amidopropionic acid is 196°; it is given by Beilstein as 180°, and has been found by E. Mulder (*Ber.*, **9**, 1902) to be 190°. The substance formed by the action of the hypobromite on the imide is

$$NKBr\cdot CO\cdot CH_2\cdot CH_2\cdot COOH,$$

and in alkaline solution this undergoes transformation as follows:—

$$NKBr\cdot CO\cdot CH_2\cdot CH_2\cdot COOK + 2KHO = K_2CO_3 + KBr + NH_2\cdot CH_2\cdot CH_2\cdot COOK.$$

The authors suppose that the salt $COBr\cdot NK\cdot C_2H_4\cdot COOK$ is formed as an intermediate product (see *Rec. Trav. Chim.*, **8**, 173). Phthalimide undergoes a similar reaction with the production of anthranilic acid. The imide is heated with alkaline hypobromite and potash at 80°, the resulting product is acidified with acetic acid, and the insoluble copper salt precipitated with copper acetate. The copper salt is suspended in water, and decomposed by hydrogen sulphide. The anthranilic acid obtained is 85 per cent. of that required by theory. The mechanism of the reaction is analogous to that described above, the compound $NKBr\cdot CO\cdot C_6H_4\cdot COOK$ being first formed and then decomposing. Phthalimide reacts in like manner with other alkaline or alkaline-earthy hypobromites or with hypochlorites. The identity of the acid prepared with orthamidobenzoic acid was proved.

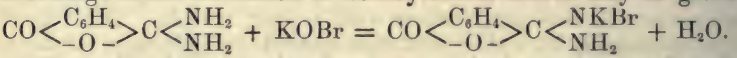
The sulphate of anthranilic acid crystallises with 1 mol. H_2O, not 2 mols. as usually stated. The anthranilic acid obtained from phthalimide is nearly pure It may be further purified by crystallisation from water, but then becomes somewhat yellow in colour. A better method of purification consists in the recrystallisation of the sulphate from alcohol and the decomposition of the salt by the exact quantity of baryta solution of known strength. Liebig's method of recrystallising the calcium salt from water and decomposing it with acetic acid yields a very pure product. Solutions of anthranilic acid generally exhibit fluorescence; this becomes less marked on further purification, but is again intensified on exposure to light.

The retarding effect on alcoholic and acetic fermentations exercised by anthranilic acid is much inferior to that of salicylic acid. It requires from 3 to 5 parts of anthranilic acid to exert the same effect on the lactic fermentation as 1 part of salicylic acid. As the artificial salicylic acid of commerce is often contaminated with impurities which modify its therapeutic properties (see *Pharm. J. Trans.*, Nov., 1890, and Fischer, *Pharm. Zeit.*, 1889, 42), the easy transformation of anthranilic acid into a very pure salicylic acid by nitrous acid becomes of some importance.

Phthalodiamide, treated with hypochlorite or, preferably, hypobromite in the same manner, yields benzoylenecarbamide. After heating at 80°, a current of carbonic anhydride is passed, and the carbamide deposited is recrystallised from glacial acetic acid. It is found to be identical with the benzoylenecarbamide prepared by Griess' method. If 2 mols. of hypobromite be employed to 1 of phthalodiamide, a benzoylenecarbamide bromide is obtained. The transformation of phthalodiamide into benzoylenecarbamide may be interpreted by the use of either the symmetrical or the unsymmetrical formula for the amide; Wislicenus' results (*Annalen*, **242**, 40) render the latter probable.

The phthalimide reaction described above leaves open the question of the constitution of this imide; the ease with which phthalimide may be converted into an amide renders it probable that the amide and the imide possess an analogous constitution. Sandmeyer's experiments support the unsymmetrical formula (*Ber.*, **18**, 1499); those of Kuhara (*Amer. Chem. J.*, **3**, 26) and Auger (*Bull. Soc. Chim.* [2], **49**, 345) rather lead to its rejection. The authors have undertaken researches for the purpose of settling the constitution of phthalimide and its isomerides.

Assuming the unsymmetrical constitution for phthalodiamide, the first stage in the formation of benzoylenecarbamide may be given as

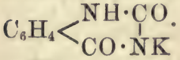


$$\mathrm{CO}{<}^{\mathrm{C_6H_4}}_{-\mathrm{O}-}{>}\mathrm{C}{<}^{\mathrm{NH_2}}_{\mathrm{NH_2}} + \mathrm{KOBr} = \mathrm{CO}{<}^{\mathrm{C_6H_4}}_{-\mathrm{O}-}{>}\mathrm{C}{<}^{\mathrm{NKBr}}_{\mathrm{NH_2}} + \mathrm{H_2O}.$$

A similar molecular migration has been noticed previously (*Rec. Trav. Chim.*, **9**, 37) to that which now takes place in the alkaline solution, with formation of potassium orthoureidobenzoate,

$$COOK\cdot C_6H_4\cdot NH\cdot CONH_2.$$

This salt is unstable, and readily suffers transformation, even in alkaline solution, into the potassium salt of benzoylenecarbamide,



$$\mathrm{C_6H_4}{<}^{\mathrm{NH\cdot CO}}_{\mathrm{CO\cdot NK}}.$$

When dilute hydrochloric acid is added to a solution of phthalyl chloride in excess of ammonia, prepared in the cold, a substance is obtained isomeric with phthalimide. This β-imide has acid properties, dissolves in solution of potassium carbonate with evolution of carbonic anhydride, and is reprecipitated on adding hydrochloric acid to the solution. Boiling water decomposes it readily. Its melting point is generally found between 180° and 190°; when heated further, the mass melts, resolidifies, and is transformed into the α-imide (ordinary phthalimide). W. T.

Reduction of Trimethylgallamide; Acetylgallamide. By M. Marx (*Annalen*, **263**, 249—259; compare Hutchinson, this vol., p. 561). —*Trimethylgallamide*, $C_6H_2(OMe)_3\cdot CONH_2$, can be prepared by gradually adding a concentrated solution of potash (3 mols.) in methyl alcohol to a boiling mixture of methyl alcohol and methyl iodide (3 mols.) in which pure gallamide is suspended; it crystallises from dilute alcohol in colourless, lustrous prisms, melts at 176—177°, and is only sparingly soluble in water, but more readily in ether, alcohol, and chloroform; it is not acted on by mineral acids in the cold, but it is converted into trimethylgallic acid (m. p. 168—170°) by boiling soda.

Trimethylgallyl alcohol, $C_6H_2(OMe)_3{\cdot}CH_2{\cdot}OH$, is obtained, together with hexamethoxybenzile, and probably also the corresponding hydrobenzoïn, when trimethylgallamide (20 grams) is reduced with $2\frac{1}{2}$ per cent. sodium amalgam (1 kilo.) in alcoholic solution, dilute sulphuric acid being constantly added in order to keep the solution acid; when reduction takes place in strongly acid solution, the alcohol is the principal product, but in only slightly acid solution the best yield of the benzile is obtained; in alkaline solution, brown, resinous products are formed. The solution is filtered from the precipitated hexamethoxybenzile, evaporated until free from alcohol, filtered again to separate the crystals of hexamethoxybenzoïn, and then extracted with ether; on evaporating the ethereal solution, the alcohol remains as an oil, mixed, however, with a little of the benzoïn, from which it is separated by solution in a small quantity of ether. It is a yellowish oil, boils at 228° under a pressure of 25 mm., and is very readily soluble in alcohol, ether, and benzene, but only very sparingly in cold water; it dissolves in concentrated sulphuric acid with a deep-red coloration, and it is completely destroyed by concentrated hydrochloric acid at 100°.

Hexamethoxybenzile, $C_6H_2(OMe)_3{\cdot}CO{\cdot}CO{\cdot}C_6H_2(OMe)_3$, crystallises in yellow, lustrous needles, melts at 189°, and is insoluble in water and alkalis, and only sparingly soluble in cold alcohol, but more readily in ether, chloroform, benzene, and glacial acetic acid. It dissolves in concentrated sulphuric acid with a bluish-green coloration which soon becomes of a lighter shade; it is not decomposed by boiling concentrated hydrochloric acid, and it combines with phenylhydrazine and with hydroxylamine.

Hexamethoxybenzilic acid, $OH{\cdot}C[C_6H_2(OMe)_3]_2{\cdot}COOH$, can be obtained by melting the preceding compound with potash, but is best prepared by boiling it with 5 per cent. potash for about six hours. It crystallises from water in long, colourless prisms, melts at 175° with decomposition, and is readily soluble in alcohol, ether, and benzene, but only sparingly in water; with concentrated sulphuric acid, it gives a deep-blue coloration which soon changes to a dirty-green.

Hexamethoxydeoxybenzoïn, $C_6H_2(OMe)_3{\cdot}CO{\cdot}CH_2{\cdot}C_6H_2(OMe)_3$, prepared by reducing hexamethoxybenzile with zinc-dust and acetic acid, crystallises from dilute alcohol in long, colourless needles, melts at 161—162°, and is insoluble in cold water and alkalis, but readily soluble in alcohol, ether, and chloroform; it dissolves in concentrated sulphuric acid, yielding a deep-red solution which quickly turns yellowish-brown. The corresponding *hydrobenzoïn*, obtained in the preparation of trimethylgallyl alcohol, crystallises from dilute alcohol in colourless needles, melts at 217°, and is insoluble in water and alkalis; it does not reduce Fehling's solution, and it dissolves in concentrated sulphuric acid with a deep-blue coloration which disappears after some hours' time.

Tetracetylgallamide, $C_{15}H_{15}NO_8$, is deposited in crystals when gallamide (10 grams) is dissolved in warm acetic anhydride (50 grams), the solution heated for a few minutes, and then allowed to cool, crystallisation being promoted by rubbing; it separates from alcohol in colourless, lustrous prisms, melts at 210°, and is only sparingly soluble in benzene, alcohol, light petroleum, and glacial acetic acid, and insoluble in water and ether; it is decomposed by cold soda and by boiling water. The *triacetyl* derivative, $C_{13}H_{13}NO_7$, is obtained when the filtrate from the tetracetyl derivative is repeatedly evaporated with alcohol; it crystallises from water in colourless prisms, melts at 163°, and is moderately easily soluble in alcohol, but only sparingly in water, and insoluble in ether; it is probably identical with the impure acetyl derivative (m. p. about 150°) described by Schiff and Pons (Abstr., 1885, 796). F. S. K.

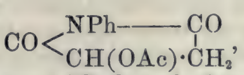
Acids of the Fumaric Series. By C. A. Bischoff (*Ber.*, **24**, 2001—2025).—The compound obtained by heating malic dianilide with acetic anhydride, to which the formula $C_{32}H_{28}N_4O_4$ was given (Abstr., 1890, 1162), is now identified as fumaric dianilide, $C_{16}H_{14}N_2O_2$, since it is obtained from fumaric dichloride by the action of aniline, yields Anschütz's fumaranilic acid (m. p. 230—232°), the so-called diphenyl-$\alpha\gamma$-diketopiperazine-$\beta\delta$-homocarboxylic acid of the author and Nastvogel (*loc. cit.*), when heated with 10 per cent. alcoholic potash (2 mol. prop.) in a reflux apparatus for three hours, and is converted into fumaric acid by treatment in amyl alcohol solution with sodium. The constitution of fumaric diparatoluidide (*loc. cit.*) has been confirmed by its synthesis from fumaric dichloride and paratoluidine.

The substance left undissolved when the product of the action of acetic anhydride on malic α-dinaphthalide is extracted successively with acetic acid, dilute ammonia, and water, and provisionally regarded as the acetyl derivative, $C_{26}H_{22}N_2O_4$ (*loc. cit.*), consists of about 40 per cent. of the acetyl derivative and 60 per cent. of fumaric α-dinaphthalide, and is separated into its constituents by extraction with alcohol, in which the former is soluble and the latter insoluble.

Acetomalic α-dinaphthalide,

$$C_{10}H_7 \cdot NH \cdot CO \cdot CH(OAc) \cdot CH_2 \cdot CO \cdot NH \cdot C_{10}H_7,$$

melts at 232°, and, when heated in an oil-bath at 240—250°, decomposes into acetic acid and fumaric α-dinaphthalide; hence the proportion of the two constituents in the above product is dependent on the duration and temperature of the reaction. *Fumaric α-dinaphthalide*, $C_{24}H_{18}N_2O_2$, does not melt below 360°, and is practically insoluble in all the ordinary solvents, and only sparingly soluble in nitrobenzene or aniline. On treatment with 10 per cent. alcoholic potash, it yields fumaric acid, α-naphthylamine, and a small quantity of a compound which crystallises from acetone in slender needles, and consists probably of fumaronaphthylic acid. Piperazine derivatives, therefore, are not obtained by the action of acetic anhydride on malic dianilide and its homologues, and the further investigation of these compounds has been abandoned.

Acetomalanil,

$CO<\begin{matrix}NPh\text{——}CO\\ \vert\\ CH(OAc)\cdot CH_2\end{matrix}$, obtained by digesting malanil dissolved in benzene with the calculated quantity of acetic chloride, is a colourless, crystalline substance which melts at 137°, and is readily soluble in most solvents, but very sparingly soluble in cold water. *Acetomalic β-naphthil*, $C_{16}H_{13}NO_4$, prepared in like manner from malic β-naphthil (*loc. cit.*), crystallises in colourless scales, and melts at 116°.

In an earlier paper, it has been shown that mesaconic and citraconic acids can be prepared from ethyl chloropropenyltricarboxylate (Abstr., 1890, 1101); the preparation of homologues of these acids from ethyl chlorobutenyltricarboxylate is now described.

When ethylic chlorobutenyltricarboxylate is hydrolysed by prolonged boiling with equal weights of hydrochloric acid (sp. gr. 1·2) and water, it is for the most part converted into ethylmaleic acid.

Ethyl sodiobutenyltricarboxylate is prepared by the action of sodium wire (6·9 grams) on a solution of ethyl butenyltricarboxylate (82 grams) in absolute ether (375 c.c.), and when the solution is treated with a 10 per cent. iodine solution (about 72 grams of iodine) until the colour no longer disappears, and the product is subsequently saponified with baryta, a mixture of ethylsuccinic acid and ethylmaleic acid is obtained.

Bromethylsuccinic acid (m. p. 202°), or the impure acid melting at 185°, obtained by the action of bromine on butenyltricarboxylic acid (this vol., p. 291), is converted into a mixture of ethylfumaric and ethylmaleic acids by boiling in a reflux apparatus for two days with about three times its weight of concentrated hydrochloric acid. Both the isomeric bromethylsuccinic acids (*loc. cit.*), on warming with an equal weight of caustic potash dissolved in five times its weight of alcohol, yield ethylmaleic acid.

Ethylsuccinic acid (15 grams), on careful bromination in a reflux apparatus at 200° with bromine (16 grams), distillation of the product, and conversion of the resulting anhydride into acid by treatment with barium carbonate and subsequent addition of hydrochloric acid to the concentrated filtrate, yields ethylmaleic acid, free from methylitaconic acid and products of higher melting point.

When ethylsuccinic anhydride (36 grams) is heated with chloroform (40 grams) and bromine (46 grams) for five hours at 130—140°, it is converted into bromethylsuccinic anhydride, and this, when heated at 180°, begins to decompose with the elimination of carbonic anhydride, and, on distillation at 220—250°, evolves hydrogen bromide in large quantity, yielding a yellow, oily distillate (28 grams) containing methylitaconic acid and ethylmaleic acid. Ethylfumaric acid is not formed in the reaction.

Ethylmaleic acid, obtained by these methods, is identical in properties with Fittig and Fränkel's methylcitraconic acid (Abstr., 1890, 585), and ethylfumaric acid is identical with the oxypentic acid of Demarçay (compare Walden, this vol., p. 1187).

Attempts to prepare dimethylfumaric acid by intramolecular change from the maleïnoïd form being unsuccessful, experiments have been made with the object of preparing it by other methods, but without success. A mixture of potassium propionate and pyruvic acid, when heated at 140°, gave pyrotritartaric acid instead of dimethylfumaric acid, and the attempt to prepare Markownikoff and Krestowikoff's bibasic acid of the formula $C_6H_8O_4$ (Abstr., 1881, 1127) by the action of sodium wire on ethyl α-bromopropionate resulted in the production of so small a quantity of substance that it is as yet impossible to say whether or not this acid is dimethylfumaric acid.

Ethyl chlorobutenyltricarboxylate boils at 193° under 13 mm. pressure. Butenyltricarboxylic acid melts at 141°, instead of 119° (compare Polko, Abstr., 1888, 134), and isobutenyltricarboxylic acid at 148° instead of 120° (compare Barnstein, Abstr., 1888, 135).

W. P. W.

Action of Thiocarbimides on Hydroxylamine. By H. v. D. Kall (*Annalen*, **263**, 260—268).—Phenylhydroxythiocarbamide (compare Voltmer, this vol., p. 558) melts at 108°, and is insoluble in water, benzene, and light petroleum, and only sparingly soluble in ether, but readily in alcohol and acetone.

Carbanilidophenylhydroxycarbamide, NHPh·CO·N(OH)·CO·NHPh, separates in crystals when a 10 per cent. aqueous solution of hydroxylamine is shaken with phenylthiocarbimide at the ordinary temperature; it melts at 178° with decomposition, and is readily soluble in hot alcohol, benzene, and chloroform, but only sparingly in ether and hot water, and insoluble in light petroleum, cold water, alkalis, and dilute hydrochloric acid.

Phenylhydroxycarbamide, NHPh·CO·NH·OH, is deposited in reddish, granular crystals when phenylthiocarbimide is shaken with excess of an ice-cold solution of hydroxylamine; it separates from ether in colourless crystals, melts at 140° with decomposition, and is sparingly soluble in ether and water, but readily in hot alcohol and soda. It reduces Fehling's solution on warming, and combines readily with phenylthiocarbimide, forming carbanilidophenylhydroxycarbamide; it is decomposed by boiling 20 per cent. hydrochloric acid with liberation of hydroxylamine and formation of carbanilidohydroxycarbamide, but boiling alkalis decompose it into aniline, hydroxylamine, and carbonic anhydride.

Hydroxylamine thiocarbimide is formed when hydroxylamine sulphate is treated with barium thiocarbimide in cold, aqueous solution; when the filtered solution is warmed, sulphurous anhydride is evolved, sulphur is deposited, and ammonium sulphate, ammonium thiocarbimide, and ammonium amidosulphonate are produced.

F. S. K.

Aromatic Alkyl Ketones: their Oxidation by Potassium Permanganate. By A. Claus (*J. pr. Chem.* [2], **43**, 531—537; compare Abstr., 1890, 769, 979; this vol., pp. 199, 564).—The salts of paraxylylglycollic acid (this vol., p. 564) are characterised by their solubility; among the salts of the heavy metals, only the ferric and lead salts are precipitated by normal sodium paraxylylglycollate.

Paracymyl ethyl ketone [Me : COEt : Pr = 1 : 2 : 4] is a colourless, strongly refractive liquid; it boils at 254° (uncorr.), and is volatile with steam; it dissolves in most organic solvents, but not in water; light gradually darkens it. When this ketone is reduced in aqueous alcoholic solution by sodium amalgam, it yields the *secondary alcohol*, $C_6H_3MePr{\cdot}CHEt{\cdot}OH$, a yellowish oil which boils about 300°, and will not solidify. Complete oxidation by nitric acid or permanganate converts the ketone into 4-methylisophthalic acid, showing that the ketone group and the propyl group are in the meta-position to each other. Limited oxidation with potassium permanganate converts it into paracymylglyoxylic acid (this vol., p. 199).

Paracymyl propyl ketone [Me : COPr : Pr = 1 : 2 : 4] is a colourless, strongly refractive liquid which boils at 265—266° (uncorr.), and is hardly volatile with steam. Reduction by sodium amalgam converts it into the *secondary alcohol*, $C_6H_3MePr{\cdot}CHPr^a{\cdot}OH$, an oily, yellowish liquid. Oxidation by potassium permanganate converts the ketone into paracymylglyoxylic acid. A. G. B.

Synthesis of Peonol. Application of Perkin's Reaction to Aromatic Ketones. By Y. TAHARA (*Ber.*, **24**, 2459—2462).—The substance (m. p. = 45°) isolated by Martin and Yagi (*Arch. Pharm.*, 1878, Part IV) from the root bark of *Peonia moutan*, by extraction with ether, has been recognised by Nagai (*Journ. Japan. Pharm. Soc.*, 1888, Nos. 77 and 81) as paramethoxyorthohydroxyphenyl methyl ketone, $OMe{\cdot}C_6H_3(OH){\cdot}COMe$, since it is converted into resacetophenone by hydrolysis, and its acetyl derivative, on oxidation and subsequent removal of the acetyl radicle, yields paramethoxysalicylic acid. According to Nagai, this substance, termed by him peonol, crystallises in colourless, lustrous needles of aromatic odour, melts at 50°, volatilises with steam, and is readily soluble in ether, alcohol, chloroform, benzene, and carbon bisulphide, but only sparingly in hot water. It dissolves also in caustic alkalis, forming well crystallised salts, but is insoluble in ammonia and alkaline carbonates. The solution in concentrated sulphuric acid is colourless, but that in concentrated nitric acid has an intense green colour. Ferric chloride colours the alcoholic solution dark violet. The methyl derivative crystallises in scales and melts at 40°; the acetyl derivative melts at 46·5°.

The author has synthesised peonol by the partial methylation of resacetophenone in methyl alcohol solution with methyl iodide and the theoretical quantity of caustic potash, and finds that it is the sole product of the reaction.

Nagai (*loc. cit.*) states that when peonol is heated with acetic anhydride and anhydrous sodium acetate, it yields, in addition to acetylpeonol, two isomeric substances of the composition $C_{13}H_{12}O_4$, which melt at 130° and 160° respectively. These crystallise in colourless, lustrous, flat needles, are practically insoluble in water and ether, sparingly soluble in cold alcohol, and tolerably soluble in hot alcohol and acetic acid, and can be separated by boiling with 18 per cent. acetic acid, in which the former is the more soluble. Both compounds are insoluble in cold alkalis, but dissolve with decomposition on boiling.

The author finds that the reaction of acetic anhydride and sodium acetate with peonol proceeds on the lines of the Perkin synthesis, and thus affords the first instance of the successful application of this reaction to ketones. A similar reaction is also obtained with resacetophenone, but acetophenone behaves like the majority of ketones. Details are reserved for a later communication.

W. P. W.

Derivatives of Ethyl Dinitrophenylacetate. By M. DITTRICH and V. MEYER (*Annalen*, **264**, 129—149).—*Mesityl methyl ketone*, $C_6H_2Me_3\cdot COMe$, can be obtained by warming a carbon bisulphide solution of mesitylene with acetic chloride in presence of aluminium chloride; it is a liquid boiling at 235—236°, and having a very characteristic, unpleasant smell.

Mesitylglyoxylic acid, $C_6H_2Me_3\cdot CO\cdot COOH$, is formed when mesityl methyl ketone is oxidised with an alkaline solution of potassium permanganate at 0°, as described by Glücksmann in the case of acetophenone (Abstr., 1889, 1416); it separates from hot carbon bisulphide in well-defined, yellowish crystals, melts at 112—115° with previous softening, and is only sparingly soluble in carbon bisulphide and light petroleum, but readily in most of the other organic solvents, and also in boiling water.

Mesitylacetic acid, $C_6H_2Me_3\cdot CH_2\cdot COOH$, prepared by heating the preceding compound with hydriodic acid and amorphous phosphorus at 160° for six hours, crystallises from hot water in slender needles, melts at 166—167°, and is readily soluble in most ordinary solvents, except water and light petroleum.

Dinitromesitylacetic acid, $C_6(NO_2)_2Me_3\cdot CH_2\cdot COOH$, is formed when the acid is gradually introduced into fuming nitric acid, and the solution then boiled for some time; it crystallises from dilute alcohol in slender, lustrous needles, melts at 243°, and is rather more sparingly soluble than mesitylacetic acid. The *methyl* salt crystallises from alcohol in lustrous plates, melts at 140—141°, and resembles the acid in its behaviour with solvents; it is not acted on by diazobenzene chloride or diazobenzene sulphate in presence of an aqueous solution of sodium acetate.

Dinitromesitylglyoxylic acid, $C_6(NO_2)_2Me_3\cdot CO\cdot COOH$, is best prepared by gradually adding mesitylglyoxylic acid to cold fuming nitric acid (6 parts), keeping the solution for some time, and then pouring it on ice; it crystallises from hot water in slender needles; melts at 178—180°, decomposes at about 213°, and is only sparingly soluble in light petroleum, but more readily in the other ordinary solvents. The *hydrazone* crystallises from dilute alcohol in slender, yellow needles, and melts at 202° with decomposition. The *methyl* salt crystallises from alcohol in broad, lustrous needles, melts at 158—160°, and is only sparingly soluble in alcohol, ether, and light petroleum, but more readily in benzene and chloroform.

The *hydrazone*, $C_6(NO_2)_2Me_3\cdot C(N_2HPh)\cdot COOMe$, is obtained when methyl dinitromesitylglyoxylate is boiled with excess of phenylhydrazine acetate in alcoholic solution; it crystallises from alcohol in yellow needles, melts at 197—198° with previous softening, and decomposes at 210—220°. The corresponding *acid*,

$$C_6(NO_2)_2Me_3{\cdot}C(N_2HPh){\cdot}COOH,$$

is formed in small quantities when the methyl salt is boiled with concentrated potash for a short time, but most of the methyl salt remains unchanged; as, under these conditions, a condensation analogous to that which occurs in the case of the hydrazone of methyl dinitrophenylacetate (compare Meyer, Abstr., 1889, 516) does not take place, it would seem that it is the nitro-group in the ortho-position to the carbon chain which is eliminated as potassium nitrite in the formation of nitrophenylindazolecarboxylic acid from the hydrazone of methyl dinitrophenylacetate.

Pseudocuminyl methyl ketone, $C_6H_2Me_3{\cdot}COMe$, boils at 249—252°. *Pseudocumylglyoxylic acid*, $C_6H_2Me_3{\cdot}CO{\cdot}COOH$, prepared by oxidising pseudocuminyl methyl ketone by Glücksmann's method (*loc. cit.*), crystallises from light petroleum in colourless needles, melts at about 75°, and is very readily soluble in all the ordinary solvents except water and light petroleum. When treated with fuming nitric acid at −17°, it yields only resinous products; with weaker acid it is converted into a crystalline mononitro-derivative, which begins to decompose at 90° and melts at about 160°. F. S. K.

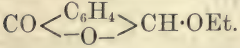
Preparation of Unsaturated Aromatic Acids. By L. Edeleano (*Bull. Soc. Chim.* [3], **5**, 170—172).—In a previous communication, the author described the preparation of cinnamic acid according to the equation

$$C_6H_5{\cdot}COH + CH_3{\cdot}COCl + nCH_3{\cdot}COONa = C_6H_5{\cdot}CH{:}CH{\cdot}COOH + CH_3{\cdot}COOH + NaCl + (n-1)CH_3{\cdot}COONa$$

(Abstr., 1890, 891). He has since succeeded in preparing phenylangelic acid by heating at 120—125° during 40 hours benzaldehyde (1 mol.), butyric chloride (1 mol.), and anhydrous sodium acetate (3 mols.), and cinnamylangelic acid by similar treatment of cinnamaldehyde, butyric chloride, and sodium acetate. The corresponding acids are separated from the crude product of the reaction by boiling it with excess of sodium carbonate solution, extraction of the alkaline solution with ether to remove oily matter and excess of aldehyde, and decomposition of the sodium salt with hydrochloric acid. In the preparation of cinnamylangelic acid, a yellow substance melting at 90° is formed, which the author intends studying. The general formula for this reaction becomes:—$R{\cdot}COH + R'CH_2{\cdot}COCl + nCH_3{\cdot}COONa = R{\cdot}CH{:}CR'{\cdot}COOH + CH_3{\cdot}COOH + NaCl + (n-1)CH_3{\cdot}COONa$.

T. G. N.

Action of Potassium Cyanide on Phthalaldehydic Acid. By C. Graebe and A. Landriset (*Ber.*, **24**, 2296—2297).—Diphthalyl is formed by the action of potassium cyanide on ethyl phthalaldehydate. The best results are obtained by warming a mixture of equal weights of the ethereal salt, potassium cyanide, and alcohol (95 per cent.). The yield amounts to 15 per cent. of the ethereal salt employed. The results agree with those of Goldschmidt and Egger (*Monatsh.*, **12**, 49), and the authors, like these chemists, assume that the ethereal salt of phthalaldehydic acid here acts in its tautomeric form,



$$CO<\overset{C_6H_4}{\underset{-O-}{}}>CH\cdot OEt.$$

In aqueous solution, the reaction takes place in a different way, and benzoïndicarboxylic acid is formed. Phthalaldehydic acid was heated with 12—15 per cent. of potassium cyanide in aqueous solution for 20—30 minutes. The product, which is entirely soluble in sodium carbonate, was purified by means of the barium salt. The acid obtained from it is insoluble in cold water and ether, sparingly soluble in hot water, decomposes at 112°, and gives diphthalylic acid on oxidation with permanganate. Only a small yield of the benzoïndicarboxylic acid is obtained. E. C. R.

Method for the Isolation of Aromatic Sulphonic Acids. By L. GATTERMANN (*Ber.*, **24**, 2121—2122).—Instead of the very troublesome method usually adopted for the isolation of aromatic sulphonic acids from the crude product of sulphonation, namely, by means of the barium, calcium, or lead salt of the acid, it is possible in many cases to effect a rapid and complete separation of the desired compound by first treating the crude product with water and then adding sodium chloride until the solution is saturated, when the sodium salt of the acid is deposited in crystals. This method can be very suitably employed for the isolation of benzene-, toluene-, xylene-, and mesitylene-sulphonic acids; it also gives good results in the case of phenolparasulphonic acid, phenoldisulphonic acid, and the metasulphonic derivatives of benzoic acid. A process of this kind is used to a considerable extent in the commercial preparation of certain sulphonic acids. F. S. K.

Action of Iodine in Presence of Sulphuric Acid on Calcium Benzenesulphonate. By ISTRATI and GEORGESCO (*Bull. Soc. Chim.* [3], **5**, 162—164).—Calcium benzenesulphonate (500 grams), iodine (50 grams), and sulphuric acid (1500 c.c.) were boiled together for 64 hours, iodine (40 grams) and sulphuric acid (300 c.c.) being added in the interval. From the products of the reaction, iodobenzene, paradiiodobenzene, tetra-iodobenzene, a franceïne and an iodo-derivative of calcium benzenesulphonate, $C_6H_4(SO_3)_2Ca$, were separated (compare previous abstract). T. G. N.

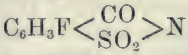
Derivatives of Benzoic Sulphinide. By R. DE ROODE (*Amer. Chem. J.*, **13**, 217—232).—A comparative study of the parahalogen derivatives of benzoic sulphinide, having especial regard to their flavours. Paranitrotoluene was converted successively into paranitrotoluene-, paratoluidine-, and paradiazotoluene-sulphonic acids, and then into the corresponding halogen sulphonic acids, sulphonic chlorides, and sulphonamides.

Parafluorotolueneorthosulphonic acid, $C_6H_3MeF\cdot SO_3H$ [$Me : SO_3H : F = 1 : 2 : 4$], is made from the diazo-acid (100 grams), by dissolving it in concentrated hydrofluoric acid (500 c.c.), and heating until nitrogen ceases to be evolved. The *calcium* and *barium* salts were prepared; the latter, $Ba(C_7H_6O_3SF)_2 + H_2O$, crystallising in small, glistening scales; the *potassium* salt, with 2 mols. H_2O, forms similar but larger scales, very soluble in water. *Parachlorotolueneorthosulphonic acid* is made in a similar manner; the *barium* and *potassium* salts were prepared, the latter crystallising in light-yellow needles. *Parabromotolueneorthosulphonic acid* is formed in like manner; the *barium* and *potassium* salts were prepared; the latter crystallises in thin, lustrous scales. *Paraiodotoluenesulphonic acid* is made by treating the diazo-acid (50 grams), in the presence of alcohol (250 c.c.) and in the cold, with successive small quantities of concentrated hydriodic acid (57 grams). When the evolution of nitrogen ceases, the alcohol is distilled off, and the acid converted into the lead and potassium salts.

The dry potassium salts thus obtained are converted into the sulphochlorides and sulphonamides by successive treatment with phosphorus pentachloride and ammonia. *Parafluorotoluenesulphonamide*, $C_6H_3MeF\cdot SO_2NH_2$ [$Me : SO_2NH_2 : F = 1 : 2 : 4$], is made by treating potassium fluorotoluenesulphonate (50 grams) with phosphorus pentachloride (100 grams). The sulphonic chloride at first obtained is allowed after purification to drop slowly into strong aqueous ammonia (1 litre). The sulphonamide separates out as a bright-yellow solid, which dissolves easily in water and alcohol, and crystallises from these menstrua in large, transparent prisms, or long, white needles, and melts at 155°.

The sulphonamides are converted into the sulphinides by oxidation with alkaline permanganate. The amide (20 grams) is dissolved in water (2 litres) rendered alkaline with potash (8 grams), and the solution is kept at a boiling temperature while potassium permanganate (35 grams) in concentrated aqueous solution is gradually added. The sulphinide is precipitated from the colourless solution by hydrochloric acid, and purified by conversion into the calcium salt. The salts thus prepared form radial groups of white needles, and taste like the sulphinides. They all crystallise with 7½ molecules of water.

The pure sulphinides are precipitated by hydrochloric acid from the aqueous solutions of their salts.

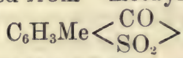


The *parafluorosulphinide*, $C_6H_3F<\genfrac{}{}{0pt}{}{CO}{SO_2}>NH$ [$CO : SO_2 : F = 1 : 2 : 4$], crystallises from its aqueous solution in colourless needles or rhombs, and melts at 200°. It is very sweet, with a somewhat bitter after-taste.

The *parachlorosulphinide* crystallises from its aqueous solution in pearly scales, and melts at 218°. It is decidedly sweet, with a very bitter after-taste. When boiled with dilute hydrochloric acid in a reflux apparatus, it is converted into *acid ammonium parachlororthosulphobenzoate*.

The *parabromosulphinide* is somewhat sweet, with a decidedly bitter after-taste.

The *paraiodosulphinide* crystallises from a hot aqueous solution in fine, white needles melting at 230°. It is not at all sweet, and only slightly bitter. Jn. W.



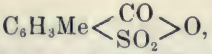
Orthosulphoparatoluic Acid and its Derivatives. By W. W. Randall (*Amer. Chem. J.*, **13**, 256—273).—The various substances were prepared from "methylsaccharin" (paratoluic or methylbenzoic sulphinide), $C_6H_3Me{<}{\genfrac{}{}{0pt}{}{CO}{SO_2}}{>}NH$ [CO : SO_2 : Me = 1 : 2 : 4], made from paratoluidine by the method of the Badische Anilin- und Sodafabrik (Abstr., 1890, 382).

"*Methylsaccharin*" (*loc. cit.*) crystallises from water in fine, white needles, having the composition $C_8H_7NSO_3 + 1\frac{1}{2}H_2O$; it is slightly soluble in cold water and ether, readily in hot water and alcohol. At 190° it loses its water of crystallisation, and then gradually sublimes and decomposes; it melts at 249°. In taste it is at first intensely sweet, but afterwards bitter. It acts as a monobasic acid, the imido-hydrogen being replaceable. The *barium* salt, $Ba(C_8H_6NSO_3)_2 + 5H_2O$, crystallises from its aqueous solution in the triclinic form. The *calcium* salt crystallises in opaque, white needles, exceedingly soluble in water. The *silver* salt, $AgC_8H_6NSO_3 + 1\frac{1}{2}H_2O$, forms colourless, diamond-shaped, highly refractive crystals, soluble in water.

Orthosulphoparatoluic acid,

$$COOH{\cdot}C_6H_3Me{\cdot}SO_3H \quad [COOH : SO_3H : Me = 1 : 2 : 4],$$

is prepared by heating "methylsaccharin" (25 grams) with dilute hydrochloric acid (100 c.c. acid and 500 c.c. water) in a reflux apparatus until it is all dissolved. The ammonium hydrogen orthosulphoparatoluate, $COOH{\cdot}C_6H_3Me{\cdot}SO_3NH_4$, which crystallises out, is treated with twice its weight of phosphorus pentachloride, and the mixture heated at 120° to drive off the phosphorus oxychloride formed. *Orthosulphoparatoluic chloride*, $COCl{\cdot}C_6H_3Me{\cdot}SO_2Cl$, thus obtained, forms crystals which melt at 59°, and are soluble in ether and light petroleum. It is converted into the acid by heating with water in a reflux apparatus. Orthosulphoparatoluic acid crystallises with $3\frac{1}{2}$ mols. H_2O in tetragonal prisms which are soluble in water, alcohol, and ether; the water of crystallisation is lost at 135°, and the anhydrous acid melts at 158°. It is bibasic, forming stable normal, and acid salts, which are not decomposed by boiling with strong alkalis, as stated by Fittica (*Liebig's Annalen*, **172**, 328—329). The *potassium* salt is very soluble in water, and is converted by fusion with caustic potash into the potassium salt of orthohydroxyparatoluic acid [COOH : OH : Me = 1 : 2 : 4]. The free acid is thrown down from the aqueous solution of the salt on the addition of hydrochloric acid. It melts at 177·5° (corr.), is readily soluble in hot water, almost insoluble in cold, and with ferric chloride gives an intense, violet coloration. The *ammonium* salt, $(NH_4)_2C_8H_6SO_5 + 2\frac{1}{2}H_2O$, is very soluble in water. The *barium* salt, $BaC_8H_6O_5$, forms fine, white needles. The *calcium* salt, $CaC_8H_6O_5 + H_2O$, crystallises in colourless prisms, which lose water at 255°; the anhydrous salt is hygroscopic. The *magnesium* salt is deposited from its aqueous solution as a yellowish, gummy mass, but from alcoholic solution as a white, deliquescent, crystalline paste. The *silver* salt, $Ag_2C_8H_6O_5 + 1\frac{1}{2}H_2O$, is deposited from weak aqueous solution in colourless rhombohedra, but from concentrated solutions as a yellow, amorphous precipitate. It is only slightly soluble in water. The *acid potassium* salt, $KC_8H_7SO_5$, forms rhombic prisms soluble in water. The *acid ammonium* salt is formed during the preparation of the acid as above. The acid barium salt, $Ba(C_8H_7SO_5)_2 + 4H_2O$, crystallises from aqueous solution in long, colourless, efflorescent needles. The *acid calcium* salt, $Ca(C_8H_7SO_5)_2 + 4H_2O$, is very soluble in water, and crystallises in thin, cubical plates. The *acid magnesium* salt is very soluble in water.



Orthosulphoparatoluic anhydride, $C_6H_3Me\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle O$, appears to be formed when the dehydrated acid is heated with phosphoric anhydride at 145°. It forms a brilliant, fluorescent compound with resorcinol.

JN. W.

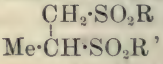
Hydrolysis of Sulphones. By R. OTTO (*Ber.*, **24**, 1832—1836); compare Stuffer, Abstr., 1890, 987, and this vol., p. 180; also Autenrieth, this vol., pp. 540 and 1067). Trimethylene diphenylsulphone (m. p. 127—128°) is not acted on by boiling concentrated aqueous or alcoholic potash, but when heated with alcoholic potash at 115—120°, it is moderately easily decomposed into benzenesulphinic acid and a compound $O(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SOPh)_2$; the latter crystallises from alcohol in well-defined, hexagonal plates, melts at 85°, and is insoluble in water, but soluble in alcohol, ether, and chloroform.

Trimethyleneditolylsulphone, prepared by treating trimethylene bromide with sodium tolueneparasulphinate, crystallises from alcohol in lustrous plates melting at 124—125°; when heated with alcoholic potash at 115—120°, it is decomposed into toluenesulphinic acid and *ditolylsulphonepropyl ether*, $O(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}C_7H_7)_2$, a crystalline compound melting at 79—80°.

A *trisulphone* of the constitution $SO_2Ph{\cdot}CH_2{\cdot}CH(SO_2Ph)_2$ can be obtained by treating sodium thiophenate with chlorethylene chloride, and oxidising the product with potassium permanganate; it separates from alcohol in small crystals, melts at 85—86°, and is completely decomposed by dilute potash, yielding benzenesulphinic acid.

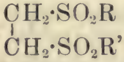
F. S. K.

Hydrolysis of Sulphones and Ethereal Salts of Benzenesulphinic Acid. By E. BAUMANN (*Ber.*, **24**, 2272—2277.—The author discusses the results obtained by Stuffer, Otto, and Autenrieth. Stuffer (Abstr., 1890, 987; this vol., p. 180) has shown that those disulphones in which the sulphone groups are combined with neighbouring carbon atoms are easily hydrolysed by dilute potash with formation of sulphinic acids. These sulphones are sharply distinguished from the sulphones which are not capable of hydrolysis, or are hydrolysed only with difficulty. To the latter belong the disulphones which, like sulphonal, contain the sulphone groups combined with the same carbon atom, or, like trimethylene disulphone, contain the sulphone groups combined with carbon atoms which are not neighbouring. Thus, propylene disulphone,



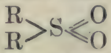
$\begin{array}{l}CH_2\cdot SO_2R\\ |\\ Me\cdot CH\cdot SO_2R\end{array}$, and

ethylene disulphone,

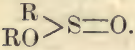


$\begin{array}{l}CH_2\cdot SO_2R\\ |\\ CH_2\cdot SO_2R\end{array}$, are easily hydrolysed when warmed with dilute potash, whilst trimethylene disulphone, $CH_2(CH_2SO_2R)_2$, is not altered by heating with concentrated aqueous or alcoholic potash on the water-bath at the ordinary pressure; only when heated in a sealed tube at 115—120° with alcoholic potash, does hydrolysis takes place.

Many sulphones have been prepared which are hydrolysed as easily as ethereal salts, and this is not without bearing on the question whether ethereal salts of sulphinic acids exist isomeric with the sulphones. Otto (Abstr., 1888, 1231; 1885, 281) has prepared a number of ethereal salts of sulphinic acids, and has come to the conclusion that sulphones are represented by the constitution



$\begin{array}{l}R\\ R\end{array}\!\!>S\!\!<\!\!\!\begin{array}{l}O\\ O\end{array}$ and the ethereal salts of sulphinic acids by the constitution



$\begin{array}{l}R\\ RO\end{array}\!\!>S{=}O$. These ethereal salts of sulphinic acids are not, however, known in a pure state. If substances like ethyl sulphone sulphonal, $CMe(SO_2Et)_2\cdot CH_2\cdot SO_2Et$, which are easily hydrolysed with production of sulphinic acids are to be accepted as ethereal salts of sulphinic acids, they must, according to Otto, have a constitution different from that of sulphonal, which is one of the sulphones most difficult to hydrolyse. This view cannot, however, be accepted until the difficultly hydrolysable compounds isomeric with the former have been prepared, which will be the true sulphones. If the ethereal salts of sulphinic acids contain quadrivalent sulphur, on oxidation, they ought to yield ethereal salts of sulphonic acids. Otto and Rössing (Trans., 1886, 710) have, indeed, described experiments in which they obtained ethereal salts of sulphonic acids from ethyl benzene- and toluenesulphinate; they did not, however, employ pure substances. The experiments of Stuffer and Autenrieth, on the other hand, show that their ethereal sulphinates, ethyl sulphone sulphonal, and similar compounds, when pure, are as stable to oxidising agents as the sulphones which cannot be hydrolysed or only with difficulty.

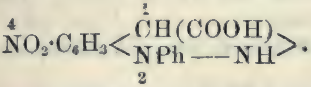
The author concludes that it is impossible to distinguish between sulphones and ethereal salts of sulphinic acids, and that the constitution of sulphinic acid is correctly represented by the formula

$\begin{array}{l}R\\ H\end{array}\!\!>S\!\!<\!\!\!\begin{array}{l}O\\ O\end{array}$. The ease with which the sulphones are hydrolysed is determined by the position of the sulphonic groups in the molecule of the organic compound, and can be compared to the unequal capacity for hydrolysis displayed by the halogen substitution products.

E. C. R.

The Synthesis of Indigotindisulphonic Acid (Indigo-carmine). By R. Knietsch (*Ber.*, **24**, 2086—2089).—Previous to the publication of Heymann's synthesis (this vol., p. 1069), the author had also observed that phenylglycocine is converted by fuming sulphuric acid into indigo-carmine; he differs, however, from Heymann with regard to the manner in which the reaction takes place. The latter supposes the formation as an intermediate product of an indoxyl sulphate, which then undergoes oxidation at the expense of the sulphuric anhydride present, whereas the author believes that the reaction proceeds in the same manner as in Heumann's synthesis with caustic potash and phenylglycocol, the elements of water being withdrawn from the latter, with formation of a leuco-compound (and in this case with simultaneous sulphonation), and that the leuco-compound is then oxidised by the oxygen of the air. The first product, like the leuco-compound obtained with caustic potash, is very unstable in acid solution; the oxidation only takes place when all free sulphuric anhydride has disappeared, and that it is really the oxygen of the air which causes this oxidation is confirmed by the fact that the surface of the mass formed in the reaction becomes blue on exposure, and that if the sulphuric acid added as a diluent is previously aërated, the yield of indigo-carmine is increased. The formation of sulphurous anhydride is readily accounted for by the subsidiary reactions which take place even under the most favourable conditions. H. G. C.

Action of Stannous Chloride on Nitrophenylindazolecarboxylic Acid. By L. Schulhöfer (*Annalen*, **264**, 149—152).—A compound of the composition $C_{14}H_{11}N_3O_4$ is formed when finely-divided nitrophenylindazolecarboxylic acid (compare Meyer, Abstr., 1889, 516) is heated with excess of an alcoholic solution of stannous chloride, and the diluted solution treated with hydrogen sulphide, filtered, and evaporated. It crystallises from hot water in colourless needles, melts at 235°, decomposes at 240°, and is soluble in acetic acid; its constitution is possibly expressed by the formula



$$\overset{4}{N}O_2\cdot C_6H_3<\begin{matrix}\overset{1}{C}H(COOH)\\ \underset{2}{N}Ph — NH\end{matrix}>.$$

F. S. K.

Benzidine Colouring Matters. By R. Brasch and G. Freyss (*Ber.*, **24**, 1958—1966).—Dimethoxydimethylbenzidine

$$[Me : NH_2 : OMe = 2 : 4 : 5]$$

is prepared from nitromethoxytoluene $[Me : NO_2 : OMe = 1 : 2 : 4]$ by reduction in the usual way. The metanitroparacresol required is obtained by dissolving 375 grams of paratoluidine in a warm mixture of 465 grams of 52 per cent. nitric acid and 1900 grams of water, cooling, adding a second 465 grams of the acid, diazotising the crystalline magma below 10° with a solution of 243 grams of sodium nitrite in 500 grams of water, and afterwards carefully warming in a reflux apparatus until the decomposition is completed. Under these conditions, the yield amounts to 78 per cent. of the theoretical. The product contains a small proportion of dinitrocresol, but this can readily be separated after methylation since nitromethoxytoluene is volatile with steam whilst dinitromethoxytoluene is not.

Azoxyparamethoxytoluene, $C_{16}H_{18}N_2O_3$, is formed when metanitroparamethoxytoluene dissolved in methyl alcohol is heated with the theoretical quantity of sodium methoxide on a water-bath for 48 hours. It crystallises from methyl alcohol in compact, sulphur-yellow prisms, melts at 148—149°, and is readily soluble in benzene, alcohol, and acetic acid.

Azoparamethoxytoluene, $C_{16}H_{18}N_2O_2$, is prepared by reducing metanitroparamethoxytoluene either in 10 per cent. methyl alcohol solution with an excess of 5 per cent. sodium amalgam, or, preferably, with the calculated quantity of stannous chloride and aqueous soda (compare Witt, Abstr., 1886, 145). It can also be obtained by adding the calculated quantity of diazotised metamidoparamethoxytoluene to a strongly alkaline solution of paracresol and methylating the resulting azo-compound. It crystallises in large, well-formed scarlet-red prisms, melts at 178—179°, is sparingly soluble in alcohol, readily soluble in acetic acid, chloroform, and benzene, and on reduction with a considerable excess of sodium amalgam is converted into metamidoparamethoxytoluene.

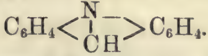
Orthodimethoxymetatolidine,

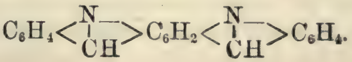
$$OMe{\cdot}C_6H_2Me(NH_2){\cdot}C_6H_2Me(NH_2){\cdot}OMe$$

[Me : NH$_2$: OMe = 2 : 4 : 5], is prepared by adding the calculated quantity of stannous chloride to a hot, hydrochloric acid solution of the azo-compound. It crystallises in silvery-white scales, melts at 156—157°, and dissolves slightly in water, but very readily in alcohol. When diazotised, it yields with β-naphtholdisulphonic acid-R., α-naphthol-α-sulphonic acid and naphthionic acid dyes which vary in shade from violet-red to red, and are almost destitute of affinity for unmordanted cotton. These results are of interest, since the tetrazo-colouring matters derived from orthodimethoxymetanisidine, like those from orthanisidine, are direct cotton dyes, whilst those from orthodimethylmetatolidine have but little affinity for unmordanted cotton (Noelting and Stricker, *Ber.*, **21**, 3138). W. P. W.

Anilidoacridines and Hydroxyacridines. By E. BESTHORN and W. CURTMAN (*Ber.*, **24**, 2039—2048).—In Bernthsen's synthesis of acridine derivatives (Abstr., 1884, 1356), diphenylamine,

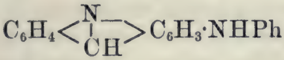
$$C_6H_5{\cdot}NH{\cdot}C_6H_5,$$

is acted on by formic acid in presence of zinc chloride, with formation of acridine,  $C_6H_4{<}\begin{matrix}N-\\|\\CH\end{matrix}{>}C_6H_4$. The authors treated diphenylmetadiamidobenzene, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_5$, in a similar manner, hoping to obtain a double acridine of the formula



$$C_6H_4{<}\begin{matrix}N-\\|\\CH\end{matrix}{>}C_6H_2{<}\begin{matrix}N-\\|\\CH\end{matrix}{>}C_6H_4.$$

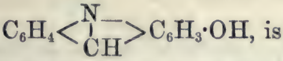
They find, however, that only one anilido-group takes part in the reaction, and that an anilidoacridine having the constitution

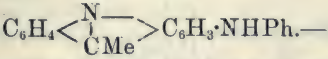


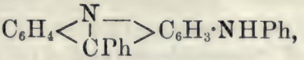
$$C_6H_4<\overset{N—}{\underset{CH}{|}}>C_6H_3\cdot NHPh$$

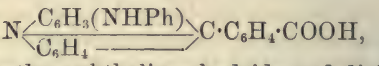
is formed. Similar compounds containing an alkyl group in the meso-position may be obtained by substituting other acids for formic acid, and all these compounds when treated with hydrochloric acid under pressure yield the corresponding hydroxy-derivatives. Whether the anilido- and hydroxy-groups occupy the ortho- or para-position to the methenyl group in the central nucleus has not yet been proved.

To prepare *anilidoacridine*, $C_{19}H_{14}N_2$, diphenylmetadiamidobenzene (5 grams), zinc chloride (10 grams), and 90 per cent. formic acid (5 grams) are heated for 4—5 hours at 250°. The product is dissolved in hot alcohol, the latter almost completely evaporated, and the residue poured into water. The red flakes which separate are warmed with very dilute sulphuric acid, and filtered from resinous matter; the sulphate separates out on cooling, and is treated with aqueous soda, extracted with ether, the extract dried with potash, evaporated, and the residue recrystallised from toluene. It forms compact, brownish-red, flat needles, melts at 175—176°, and is fairly soluble in alcohol, less readily in ether, benzene, and toluene. Its salts with mineral acids are red, and are easily soluble in alcohol, less readily in water, and almost insoluble in concentrated acids.

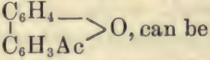
Hydroxyacridine,  $C_6H_4<\overset{N—}{\underset{CH}{|}}>C_6H_3\cdot OH$, is prepared from the foregoing compound by heating it with hydrochloric acid at 250°. The solution is made alkaline, separated from aniline by distilling in a current of steam, filtered, and treated with hydrochloric acid. The *hydrochloride* forms small, brownish-yellow needles, and when boiled with a solution of sodium carbonate yields the free hydroxyacridine in yellow, microscopic needles melting at 250°. It forms readily soluble salts with both mineral acids and alkalis, and is reduced to acridine by heating with zinc-dust.

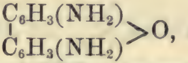
Anilidomethylacridine,  $C_6H_4<\overset{N—}{\underset{CMe}{|}}>C_6H_3\cdot NHPh$.—To prepare this compound it is best to convert the diphenylmetadiamidobenzene into the diacetyl compound and treat the latter with zinc chloride. It is purified in a similar manner to the anilidoacridine, and crystallises from toluene in fascicular aggregates of brownish-red needles, melts at 215—216°, and is readily soluble in methyl alcohol and ethyl alcohol, sparingly in ether and benzene. The corresponding *hydroxymethylacridine*, $C_{13}H_7MeN\cdot OH$, crystallises in microscopic, red needles and melts at 250°; its *hydrochloride*, $C_{13}NH_7Me\cdot OH,HCl + H_2O$, forms beautiful yellow needles.

Anilidophenylacridine,  $C_6H_4<\overset{N—}{\underset{CPh}{|}}>C_6H_3\cdot NHPh$, is obtained from dibenzoyldiphenylmetadiamidobenzene by heating it with zinc chloride, and also crystallises from toluene in fascicular aggregates of brownish-red needles. It melts at 196—197°, and dissolves readily in alcohol, ether, and benzene, the dilute, ethereal solution showing a greenish fluorescence. The corresponding *hydroxyphenylacridine*, $C_{13}NH_7Ph\cdot OH$, is a red, microcrystalline powder; its *hydrochloride*, $C_{19}H_{13}NO,HCl$, forms very lustrous, golden-yellow plates, and the *sodium* salt crystallises in a like manner.

Anilidoacridylbenzoic acid,  $N\left<\begin{array}{c}C_6H_3(NHPh)\\C_6H_4\end{array}\right>C\cdot C_6H_4\cdot COOH$, is obtained by simply heating together phthalic anhydride and diphenylmetadiamidobenzene without addition of zinc chloride. It forms small, red crystals, and is almost insoluble in the usual solvents, with the exception of acetic acid. It melts above 300°, and yields salts with mineral acids which are almost insoluble in water, but may be recrystallised from absolute alcohol. Its *sodium* salt forms white, glistening plates. When heated with hydrochloric acid at 250°, it yields *hydroxyacridylbenzoic acid*, $C_{13}NH_7(OH)\cdot C_6H_4\cdot COOH$, which melts above 250°, and has a weak basic character, forming salts which are dissociated by boiling water. Its salts with alkalis are soluble in water, the solutions showing a slight greenish fluorescence.

H. G. C.

Diphenylene Oxide. By P. GALEWSKY (*Annalen*, **264**, 187—193).—*Acetyldiphenylene oxide*,  $\left.\begin{array}{l}C_6H_4\\|\\C_6H_3Ac\end{array}\right>O$, can be obtained by gradually adding aluminium chloride to a carbon bisulphide solution of diphenylene oxide and acetic chloride; it crystallises from dilute alcohol in long, colourless needles, melts at 80—81°, boils above 350°, and is readily soluble in alcohol, ether, chloroform, light petroleum, benzene, and glacial acetic acid, but insoluble in water. The *oxime*, $C_{14}H_{11}NO_2$, crystallises from alcohol in nacreous plates or needles, melts at 145—146°, and is readily soluble in most ordinary solvents except water, in which it is insoluble. The *hydrazone*, $C_{20}H_{16}N_2O$, separates from alcohol in yellowish-brown prisms, melts at 132—133° with decomposition, and is soluble in alcohol, ether, &c., but insoluble in water.

Diamidophenylene oxide,  $\left.\begin{array}{l}C_6H_3(NH_2)\\|\\C_6H_3(NH_2)\end{array}\right>O$, crystallises from alcohol in yellow needles and melts at 188°; the *acetyl* derivative is a colourless, crystalline compound, and does not melt when heated at 320°.

F. S. K.

Condensation of Benzaldehyde with Phenols. By A. RUSANOFF (*Chem. Centr.*, 1891, i, 662; from *Bull. Acad. St. Pétersbourg*, **33**, 461—468).—The author finds that benzaldehyde forms condensation products with phenols in accordance with Baeyer's general reaction, 2 mols. of phenol and 1 mol. of aldehyde condensing with loss of 1 mol. of water. The following compounds are described:—

Paradihydroxytriphenylmethane, $CHPh(C_6H_4\cdot OH)_2$, is prepared by adding 10 grams of benzaldehyde and 17·8 grams of phenol gradually to 1—2 c.c. of sulphuric acid (4 : 1 vol. H_2O), and after allowing the mixture to cool 3—4 c.c. of the sulphuric acid is added. After remaining for several hours, the mixture is poured into water, filtered, the precipitate washed with hot water, any unchanged benzaldehyde or phenol is separated by distillation with steam, the precipitate washed with benzene, crystallised from dilute acetic acid, dissolved in alcohol, and reprecipitated by water. It crystallises in needles, melts at 160—161°, is nearly insoluble in light petroleum and carbon bisulphide, readily soluble in hot benzene, alcohol, glacial acetic acid, and chloroform, and is identical with O. Fischer and Döbner's compound. If it is warmed with bromine water, the product dissolved in alcohol, and soda solution added, a blue coloration is produced. The *diacetate*, prepared by means of anhydrous acetic acid and sodium acetate, crystallises from acetone in rhombic plates, and melts at 110—111°. The *dibenzoate*, prepared by means of benzoic chloride, crystallises in microscopic, rhombic plates, and melts at 129—130°. It is sparingly soluble in alcohol, readily soluble in ether.

Dinitrodihydroxytriphenylmethane, $C_{19}H_{12}(NO_2)_2(OH)_2$, is prepared by the action of nitric acid, sp. gr. 1·5, in glacial acetic acid solution. It crystallises from alcohol in needles, melting at 133—134°.

Phenyldithymolmethane, $CHPh(C_{10}H_{12}{\cdot}OH)_2$, prepared from benzaldehyde, thymol, and sulphuric acid, melts at 165·5—166·5°. It crystallises from alcohol and benzene with 1 mol. of the solvent, which again separates on drying. With bromine water, alcohol, and potash, it gives a blue colour reaction similar to that obtained with dihydroxytriphenylmethane. The *diacetate* is soluble in alcohol, readily soluble in chloroform and benzene, and melts at 125—126°.

J. W. L.

Oximes of Asymmetrical Ketones. By A. Schäfer (*Annalen*, **264**, 152—160).—Various asymmetrical ketones and ketonic acids have been investigated for the purpose of determining whether their oximido-derivatives exist in two isomeric modifications; it has been found that pyruvic acid, levulinic acid, acetophenone, and methyldeoxybenzoïn yield only one oxime, whereas parabromobenzophenone and paramethoxybenzophenone form two. Two methods were employed for preparing the oximes; in the one the compound was treated with hydroxylamine hydrochloride in dilute alcoholic solution; in the other, the reaction was carried out in presence of excess of soda. The behaviour of the oximes with Beckmann's mixture, and on heating with absolute alcohol at 160—170°, was also investigated.

Two oximes of the composition $C_{13}H_{10}NOBr$ are formed when a dilute alcoholic solution of parabromobenzophenone (1 mol.), hydroxylamine hydrochloride (3 mols.), and sodium hydroxide (9 mols.) is kept at the ordinary temperature until the addition of soda to a small portion of the diluted solution produces no turbidity; the two compounds can be separated by fractional crystallisation from alcohol or by the method described by V. Meyer (this vol., p. 1181).

The one melts at 165—166°, crystallises from dilute alcohol in colourless needles, and is completely decomposed by concentrated hydrochloric acid at 100°; when treated with Beckmann's mixture, it yields the anilide of parabromobenzoic acid. The *acetyl* derivative, $C_{15}H_{12}O_2NBr$, is a crystalline compound melting at 160·5°. The *benzyl* derivative, $C_{20}H_{16}ONBr$, prepared by treating the oxime with sodium ethoxide and benzyl chloride in alcoholic solution, melts at 89—90°, and is decomposed by hydriodic acid with elimination of benzyl iodide.

The second isomeride sinters together at 107°, melts at 110—111°, and crystallises from dilute alcohol in needles; it is much more readily soluble than the oxime just described, and, like the latter, it is completely decomposed by hydrochloric acid. When heated with alcohol, it is more or less completely converted into the isomeride according to the duration of the process, but it is not changed by passing hydrogen chloride into its ethereal solution. The *acetyl* derivative is crystalline, and melts at 121°. The *benzyl* derivative separates from alcohol in crystals, melts at 99—100°, and is decomposed by hydriodic acid with elimination of benzyl iodide.

The two isomeric oximes of paramethoxybenzophenone were obtained in like manner; they have recently been described by Hantzsch (this vol., p. 445). F. S. K.

Oximes of Halogenated Benzophenones. By E. HOFFMANN (*Annalen*, **264**, 160—169).—The metadibromobenzophenone obtained by brominating benzophenone (Demuth and Dittrich, this vol., p. 314) is a symmetrical compound and forms only one oxime.

Paradibromobenzophenone, $C_{13}H_8Br_2O$, prepared by treating a carbon bisulphide solution of bromobenzene with parabromobenzoic chloride in presence of aluminium chloride, separates from alcohol in colourless plates, melts at 172—173°, and is readily soluble in ether. When treated with hydroxylamine under various conditions, it yields only one *oxime;* this compound separates from dilute alcohol in slender needles, sinters together at 142°, melts completely at 149—150°, and has the composition $C_{13}H_9Br_2NO$.

Paradiiodobenzophenone, $C_{13}H_8I_2O$, is formed in small quantities when a carbon bisulphide solution of paraiodobenzoic chloride is treated with iodobenzene in presence of aluminium chloride; it crystallises from alcohol in yellowish plates and melts at 233—234°. It forms only one *oxime*, $C_{13}H_9I_2NO$, which crystallises from alcohol in slender needles and melts at 171—173°.

Iodobenzophenone, $C_{13}H_9IO$, prepared by treating benzene with iodobenzoic chloride (m. p. 77—78°) in presence of aluminium chloride, separates from alcohol in crystals melting at 102—103°; when treated with hydroxylamine in alkaline solution at the ordinary temperature, it yields two isomeric oximes of the composition $C_{13}H_{10}INO$: the one crystallises in plates, is sparingly soluble in alcohol, and melts at 178°; the other crystallises in needles, is more readily soluble, and melts at 132—134°; the latter is converted into the former when it is heated for about 12 hours at 145°.

F. S. K.

Metabromobenzophenone and its Oximes. By W. KOTTENHAHN (*Annalen*, **264**, 170—174).—*Metabromobenzophenone*, $C_6H_4Br{\cdot}COPh$, can be prepared by treating metabromobenzoic chloride with benzene in presence of aluminium chloride; it crystallises from dilute alcohol in needles and melts at 77°.

Two isomeric *oximes*, of the constitution $C_6H_4Br\cdot CPh\colon N\cdot OH$, are formed when metabromobenzophenone is treated with hydroxylamine in alkaline solution at the ordinary temperature; on diluting with a large volume of water, the α-oxime is deposited, whilst the β-compound remains in solution and can be precipitated with hydrochloric acid.

The α-oxime crystallises in colourless prisms, melts at 168°, and is decomposed into hydroxylamine and metabromobenzophenone by concentrated hydrochloric acid; when treated with Beckmann's reagent, it is converted into *metabromobenzanilide*, a colourless, crystalline compound melting at 137°. Its *acetyl* derivative,

$$C_6H_4Br\cdot CPh\colon N\cdot OAc,$$

melts at 89·5°, and its *benzyl* derivative at 73°.

The β-oxime forms large, yellow, cubic crystals, melts at 134°, and, like the α-compound, is decomposed by concentrated hydrochloric acid; when heated at about 150° for two days, it is almost completely converted into the α-oxime, and on treatment with Beckmann's mixture it is transformed into *benzoylmetabromanilide*, a crystalline compound which melts at 120°. Its *acetyl* derivative melts at 78—79°; its *benzyl* derivative crystallises from alcohol in slender needles, melts at 77°, and, like the corresponding derivative of the α-oxime, is decomposed by hydriodic acid with elimination of benzyl iodide. F. S. K.

Symmetrical Paradichlorobenzophenone and its Oxime. By M. DITTRICH (*Annalen*, **264**, 174—178; compare Demuth and Dittrich, this vol., p. 315).—Symmetrical paradichlorobenzophenone, $C_{13}H_8Cl_2$, is best prepared by gradually adding a mixture of chlorobenzene and chlorobenzoic chloride (m. p. 16°) to warm carbon bisulphide containing aluminium chloride in suspension, and then heating the whole for about two days; it crystallises from alcohol in thin, colourless plates melting at 144—145°. The *oxime*, $C_{13}H_9NOCl_2$, crystallises from alcohol in small needles, sinters together at 133°, melts at 135°, and is only moderately easily soluble in alcohol and sparingly in alkalis; when heated with concentrated sulphuric acid at 100°, it is transformed into *parachlorobenzoylparachloranilide*, $C_{13}H_9NOCl_2$, which crystallises from alcohol in thin plates melting at 207—208°. An isomeride of this oxime could not be obtained.

F. S. K.

Diphenylfurazan and some Derivatives of Oximes. By F. D. DODGE (*Annalen*, **264**, 178—187).—Diphenylfurazan, prepared by heating α-benziledioxime with water at 200—210° (compare Meyer and Auwers, Abstr., 1888, 597), melts at 94°, and distils with partial decomposition, yielding benzonitrile, phenylcarbimide, and a compound melting at 110°, which is in all probability dibenzenylazoxime, identical with the substance obtained by Beckmann by the action of sulphuric acid on α-benziledioxime.

A *dinitro*-compound, of the composition $C_{14}H_8N_2O(NO_2)_2$, is obtained, together with a substance melting at 132°, when diphenylfurazan is treated with a mixture of concentrated sulphuric acid and fuming nitric acid; it separates from glacial acetic acid in colourless crystals and melts at 218—220°.

An energetic reaction takes place when α-benziledioxime is heated with phosphorus pentasulphide; benzonitrile and small quantities of dibenzenylazoxime are formed, but diphenylfurazan is not produced. When phosphorus pentasulphide is added to a warm benzene solution of benzophenone oxime, a very energetic reaction ensues and thiobenzanilide (m. p. 101—102°) is formed.

Ammonium thiophosphate, $ONH_4{\cdot}PS(OH)_2$, is deposited in yellow crystals, mixed with sulphur, when acetoxime is treated with phosphorus pentasulphide in carbon bisulphide solution, the insoluble product extracted with alcohol, and the alcoholic solution heated to boiling; it separates from cold water in large, transparent, seemingly monoclinic prisms, melts at 146—150° with decomposition, and is readily soluble in water, but only sparingly in alcohol, and insoluble in ether and carbon bisulphide. It decomposes carbonates, gives a colourless precipitate with lead acetate, and is decomposed by hot dilute nitric acid with separation of sulphur and formation of phosphoric acid; it is also decomposed by mercuric oxide, the filtrate from the precipitated mercury sulphide giving all the reactions of phosphoric acid. F. S. K.

Tolylnaphthyl Sulphides. By E. BOURGEOIS (*Ber.*, **24**, 2264—2267).—The method of preparation consists in heating the bromotoluene with the lead salt of naphthyl mercaptan at 225° for six hours. The mixture is allowed to cool, extracted with ether, the ether evaporated off, and the product fractionally distilled in a vacuum.

Paratolyl-β-naphthyl sulphide, $C_6H_4Me{\cdot}S{\cdot}C_{10}H_7$, crystallises from dilute alcohol in small, nacreous leaflets, melts at 70·5°, boils at 237·5° under 12 mm. pressure, and is easily soluble in ether and carbon bisulphide, sparingly in alcohol.

Paratolyl-α-naphthyl sulphide crystallises from alcohol in beautiful, lustrous, clinorhombic crystals, melts at 40·5°, and boils at 233° under 12 mm. pressure.

Metatolyl-β-naphthyl sulphide crystallises from dilute alcohol in small, white needles, melts at 60°, boils at 236° under 12 mm. pressure, and is easily soluble in ether, carbon bisulphide, and acetic acid, sparingly in alcohol.

Metatolyl-α-naphthyl sulphide is a yellow, refractive oil, and boils at 229·5—230° under 12 mm. pressure.

Orthotolyl-β-naphthyl sulphide is a viscous, yellow, highly refractive oil, and boils at 232° under 12 mm. pressure.

Orthotolyl-α-naphthyl sulphide is an oil similar to the ortho-β-derivative, and boils at 231° under 12 mm. pressure. E. C. R.

Ethyl-α-naphthylamine. By E. BAMBERGER and C. GOLDSCHMIDT (*Ber.*, **24**, 2469—2472).—Ethyl-α-naphthylamine reacts in the normal way with diazo-compounds, forming azo-colours, which, on reduction with stannous chloride in hydrochloric acid solution, yield the base originally diazotised and ethyl-1 : 4-naphthylenediamine. Phenylazoethyl-α-naphthylamine has the properties described by Eicker (this vol., p. 470). *Sulphophenylazoethyl-α-naphthylamine* is a dark, carmine-red, crystalline powder of green metallic lustre, which dissolves in alcohol with a deep-red colour, in concentrated sulphuric acid with a violet colour, and in alkalis with an orange-red colour; the *sodium* salt, $C_{18}H_{16}N_3\cdot SO_3Na$, is crystalline.

Ethyl-1 : 4-*naphthylenediamine hydrochloride*, $C_{12}H_{14}N_2,2HCl$, crystallises in flat, silvery needles, melts above 300°, becomes greenish on exposure to air, and is very soluble in water, sparingly soluble in concentrated hydrochloric acid. The *base* forms colourless, oily drops, having an odour of crude α-naphthylamine, is readily soluble in hot water and the ordinary solvents, and on exposure to air and light rapidly becomes dark in colour. On treatment with hydrochloric acid, hydrogen sulphide, and ferric chloride, it gives a pale-brown colour; with aniline, potassium dichromate, and acetic acid, a brownish-red colour which on boiling becomes dark-claret; with potassium dichromate and metatolylenediamine hydrochloride, a bluish-green colour which on boiling becomes red; and with bleaching powder, a flocculent precipitate of a *chlorimide* which, on treatment with an alcoholic solution of aniline and hydrochloric acid, gives a deep-red colour. W. P. W.

αβ-**Benzenylnaphthylenediamine.** By A. Koll (*Annalen*, **263**, 313—315).—Fischer and Hepp (Abstr., 1887, 729, 1114) have shown that αβ-ethenylnaphthylenediamine is formed when β-ethylnaphthylamine is treated with amyl nitrite and an alcoholic solution of hydrogen chloride; the authors find that, under the same conditions, β-benzylnaphthylamine can be converted into αβ-benzenylnaphthylenediamine, identical with the compound prepared by Ebell (*Annalen*, **208**, 328) from β-nitrobenzonaphthylamide, and named by him anhydrobenzodiamidonaphthalene. This base separates from alcohol in colourless crystals, and from methyl alcohol in efflorescent prisms containing ½ mol. CH_4O; it melts at 214°. The *hydrochloride*, $C_{17}H_{12}N_2,HCl$, crystallises from hot alcohol in colourless needles.

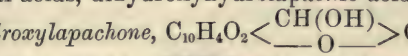
F. S. K.

Derivatives of Lapachic Acid. By S. C. Hooker (*Chem. Centr.*, 1891, i, 409; from *Proc. Franklin Inst.*, 1890, 117—124).—Bromolapachone (Abstr., 1889, 999), like lapachone, reacts with alkalis with formation of dihydroxyhydrolapachic acid. By the action of dilute mineral acids, this becomes transformed into hydroxylapachone, which, when redissolved in potash and the solution acidified with acetic acid, again forms the original acid.

Bromolapachone crystallises in two different forms, plates melting at 138·5°, and needles melting at 138°; of these, the latter appears to be the more stable, for the plates become gradually transformed into the needles. *Dihydroxyhydrolapachic acid*,

$$OH\cdot C_{10}H_4O_2\cdot CH(OH)\cdot CHPr\cdot OH,$$

melts at 181—182°, and also crystallises in two modifications, in prisms and in masses of long, thin needles. The acid forms salts which are not decomposed by carbonic anhydride. In the absence of mineral acids, dihydroxyhydrolapachic acid is stable.

Hydroxylapachone,  $\mathrm{C_{10}H_4O_2}<\begin{matrix}\mathrm{CH(OH)}\\ \mathrm{O}\end{matrix}>\mathrm{CHPr}$, forms red needles melting at 201·5°. With bromine, it forms no additive compounds, which must have been the case had it possessed the constitution ascribed to it by Paternò.

When treated with bromine in chloroform solution, lapachic acid gives five different compounds. J. W. L.

Boiling Points of some Compounds of High Molecular Weight. By R. Schweitzer (*Annalen*, **264**, 193—196).—The boiling point of anthracene was determined with the aid of Meyer and Goldschmidt's air thermometer (*Ber.*, **15**, 141, 303), and found to be 382° as the average of two experiments. The boiling points of various other organic compounds were determined, employing a mercury thermometer filled with nitrogen under pressure, and graduated to about 500°; the numbers in brackets give the boiling points found in this way. Anthracene (351°), retene (394°), phenylnaphthylcarbazole (454°), β-dinaphthylamine (483°), tribenzylamine (380—390°), β-dinaphthyl ketone (464°), α-naphthyl phenyl ketone (385°), chrysene (448°), picene (above 500°), dianthryl (above 500°), and tetrahydroxyanthraquinone (above 500°). F. S. K.

Oxidation of Alizarin-green and Alizarindigo-blue. By C. Graebe and A. Philips (*Ber.*, **24**, 2297—2299).—The authors have obtained a tri-, tetra-, and penta-hydroxyanthraquinoline from alizarin-green and alizarindigo-blue.

Trihydroxyanthraquinoline (hydroxyalizarin-blue) is contained in the portion of alizarin-green which is insoluble in nitrobenzene. It is obtained from this product by sublimation in bluish-violet needles; a good deal is, however, carbonised. It can also be obtained from the sulphonic acid contained in alizarin-green by heating it with hydrochloric acid at 180°.

Tetrahydroxyanthraquinoline is obtained in small quantities by extracting alizarin-green with nitrobenzene, and also from alizarindigo-blue by sublimation.

Pentahydroxyanthraquinoline (trihydroxyalizarin-blue) is the chief constituent of alizarindigo-blue, and may be obtained from it by crystallisation from nitrobenzene and acetic acid, or by heating the crude dye with benzoic chloride, and hydrolysing the ethereal salt thus obtained.

Alizarin-green and alizarindigo-blue, when oxidised with nitric acid (1·35), yield quinolinic acid. Alizarindigo-blue gave 50 per cent. of crude quinolinic acid; pure pentahydroxyanthraquinoline gave 52·5 per cent. Alizarin-blue sulphuric acid, obtained by the action of fuming acid on alizarin-blue, also yields quinolinic acid when oxidised with nitric acid. E. C. R.

Terpenes and Ethereal Oils. By O. Wallach (*Annalen*, **264**, 1—32).—When bromine (2 atoms) is gradually added to a well-cooled solution of anhydrous pinene (1 mol.) in dry carbon tetrachloride, the halogen is immediately absorbed, but traces of hydrogen bromide are evolved; when a further quantity (2 atoms) of bromine is added, combination takes place more or less quickly, according to the conditions of the experiment, and hydrogen bromide is again evolved; this experiment shows that pinene can combine directly with only 2 atoms of bromine. If, after adding bromine (2 atoms), the carbon tetrachloride is distilled off, a considerable evolution of hydrogen bromide is observed, and there remains a heavy, dark-coloured oil; on boiling this product with alcoholic potash for several hours, and, after evaporating the alcohol, distilling the residue with steam, a complex mixture consisting principally of camphene, pinene hydrobromide, and, perhaps, very small quantities of cymene and pinene dibromide collects in the receiver, and there remains a dark-coloured residue of pinene dibromide. The camphene obtained in this way is, doubtless, produced by the action of the alcoholic potash on pinene hydrobromide, the formation of which is due to the combination of pinene with the hydrogen bromide produced in the original reaction.

Pinene dibromide, $C_{10}H_{16}Br_2$, is easily obtained in a pure condition by dissolving the residue in alcohol, cooling the solution, and recrystallising the precipitated compound from ethyl acetate. The yield is only small, owing to the complicated nature of the original reaction, in which the bromine shows a greater tendency to substitute than to form additive products; in this respect, pinene shows a behaviour intermediate between that of aromatic hydrocarbons and that of other terpenes. Pinene dibromide is very sparingly soluble in cold alcohol, but more readily in warm ethyl acetate and chloroform, from which it separates in colourless, hexagonal crystals melting at 169—170°; it sublimes readily when heated under reduced pressure, and is optically inactive. As it cannot be obtained either from camphene or from pinene hydrobromide in the manner described above, it must be regarded as formed directly by the combination of bromine with pinene; when heated with aniline at 180° for two hours, it is converted into cymene.

When dextrorotatory limonene tetrabromide (m. p. 104—105°) is boiled with an alcoholic solution of sodium ethoxide (3 mols.) for 6—7 hours, and the solution then submitted to distillation with steam, a heavy oil collects in the receiver; this product could not be obtained in a pure condition by fractional distillation, but the results of analyses, and a study of its properties, show that it has the composition $C_{10}H_{13}Br$. It boils at 140—145° under a pressure of 13—15 mm., has a sp. gr. of 1·217 at 20°, and is dextrorotatory; it combines immediately with bromine (2 atoms), yielding an oily product, and it readily undergoes polymerisation in contact with concentrated sulphuric acid, being converted into an amorphous compound; when treated with a saturated glacial acetic acid solution of hydrogen bromide, it is converted into dipentene tetrabromide (m. p. 123°).

A further investigation of the behaviour of limonene towards bromine has shown that when 4 atoms of the halogen are employed, hydrogen bromide is invariably evolved, no matter whether the operation is carried out with moist or with anhydrous solvents.

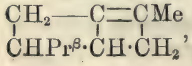
When dextrorotatory limonene tetrabromide is warmed with excess of aniline for five hours, and the solution then boiled over the free flame until the reaction is at an end, a monalkyl derivative of benzene, probably propylbenzene, cymene, and other substances, the nature of which could not be determined, are formed in small quantities.

A *tribromide* of the composition $C_{10}H_{17}Br_3$ is produced when bromine (34 c.c.) is gradually added to a solution of dipentene dihydrobromide (200 grams) in glacial acetic acid (400 c.c.) with constant shaking, any considerable rise of temperature being avoided; as soon as the colour due to free bromine has completely disappeared, alcohol (300 c.c.) is added, and the solution is kept at a low temperature for 24 hours, when the tribromide is partially deposited in crystals; the oily mother liquors are mixed with water, the precipitated oil washed with water, treated with an equal volume of methyl alcohol, and the solution placed in a freezing mixture, when a second crop of crystals is deposited; a further quantity of the crystalline product can be obtained by repeating the process. This tribromide is precipitated from its solution in hot ethyl acetate on the addition of methyl alcohol, in colourless, lustrous plates, which melt at 110°, and decompose at a higher temperature with evolution of hydrogen bromide.

A *hydrocarbon* of the composition $C_{10}H_{14}$, isomeric with cymene, is formed when the tribromide (50 grams) just described is boiled for about 15 minutes with a solution of sodium (12 grams) in alcohol (150 c.c.). It is a colourless liquid boiling at 183°; its sp. gr. is 0·863 at 20°, and its refraction $n_D = 1·49693$ at the same temperature; it combines with halogen acids, yielding oily compounds. When treated with bromine in well-cooled, alcoholic glacial acetic acid solution until a permanent yellow coloration is produced, it is converted into a *tetrabromide* of the composition $C_{10}H_{14}Br_4$, which is deposited in crystals after keeping for some time. This compound separates from hot ethyl acetate in colourless, asymmetric crystals, $a : b : c = 0·39360 : 1 : 0·35557$, melting at 154—155°. The mother liquors from the tetrabromide contain small quantities of a compound melting at 103—104°, which is much more readily soluble in ethyl acetate than the tetrabromide, with which it seems to be isomeric.

Two chlorides, one having the composition $C_{10}H_{17}Cl_3$, and melting at 85—86°, the other having the composition $C_{10}H_{16}Cl_4$, and melting at 105°, can be obtained by treating dipentene dihydrochloride with chlorine; the preparation and properties of these compounds will be described in a subsequent paper. F. S. K.

Constitution of Pinene. By G. WAGNER (*Ber.*, **24**, 2187—2190). —The author criticises Wallach's explanation (this vol., p. 1078) of the mechanism of the reaction which takes place in the oxidation of oil of turpentine to pinole hydrate (pinene glycol); he considers that the constitution of pinene is probably expressed by the formula



$\begin{array}{l} CH_2\text{—}C{=}CMe \\ \,|\qquad\;\; |\quad\;\; | \\ CHPr^{\beta}\cdot CH\cdot CH_2 \end{array}$, which affords a better explanation, not only of the behaviour of pinene on oxidation, but also of various other reactions, than the formula suggested by Wallach does. F. S. K.

Derivatives of Cantharidin. By F. ANDERLINI (*Ber.*, **24**, 1993—2000).—The compound $C_{10}H_{13}NO_3$ obtained from cantharidin by the action of ammonia (Abstr., 1890, 640) is now regarded as *cantharidinimide*, $C_{10}H_{12}O_3{:}NH$. It is not affected by prolonged boiling with caustic alkalis or baryta, yields a series of alkyl derivatives, and, when heated with acetic anhydride at 230° for about 30 hours, is converted into a crystalline *acetyl* derivative, $C_{10}H_{12}O_3{:}NAc$, which dissolves readily in alcohol, ether, and benzene, and is hydrolysed by boiling with water or aqueous alcohol.

Cantharidin methylimide, $C_{10}H_{12}O_3{:}NMe$, is obtained when cantharidin is heated with a slight excess of methylamine in methyl alcohol solution at 140—145° for 5—6 hours, and when cantharidinimide is heated with the calculated quantity of sodium carbonate, an excess of methyl iodide, and 10—12 times the amount of methyl alcohol at 100°. It crystallises from water in long, colourless, rhombic needles, $a : b : c = 0{\cdot}57497 : 1 : 0{\cdot}74685$, and melts at 125°.

Cantharidin ethylimide, $C_{10}H_{12}O_3{:}NEt$, prepared either from cantharidin or cantharidinimide, crystallises in colourless, rhombic forms, $a : b : c = 0{\cdot}52346 : 1 : 0{\cdot}78677$, melts at 105°, and is readily soluble in the ordinary solvents.

Cantharidin amylimide, $C_{10}H_{12}O_3{:}NAy$, crystallises with difficulty, melts at 46°, and is soluble in alcohol, ether, and benzene, insoluble in water.

Cantharidin allylimide, $C_{10}H_{12}O_3{:}NC_3H_5$, crystallises in monoclinic forms, $a : b : c = 0{\cdot}28226 : 1 : 0{\cdot}59433$, $\beta = 67° 35'$, melts at 80°, and is soluble in water.

Cantharidin phenylimide, $C_{10}H_{13}O_3{:}NPh$, crystallises in monoclinic forms, $a : b : c = 2{\cdot}7798 : 1 : 1{\cdot}9818$, $\beta = 89° 40'$, melts at 129°, and is readily soluble in alcohol, ether, and benzene, but insoluble in water.

Cantharidin α-naphthylimide, $C_{10}H_{13}O_3{:}NC_{10}H_7$, crystallises from acetone in lustrous, monoclinic forms, $a : b : c = 0{\cdot}55814 : 1 : 1{\cdot}75340$, $\beta = 83° 59'$, and is readily soluble in the ordinary solvents, but insoluble in water.

In addition to the methods already described for that purpose (compare Homolka, Abstr., 1886, 723), cantharic acid can also be prepared by dissolving cantharidin in 5 times the quantity of chlorosulphonic acid, and, after four hours, pouring the solution on to ice, neutralising with barium carbonate, and treating the filtrate with the requisite quantity of dilute sulphuric acid. Cantharic acid crystallises in rhombic forms, $a : b : c = 0{\cdot}96218 : 1 : 0{\cdot}68658$, and its oxime (Homolka, *loc. cit.*) in monoclinic forms, $a : b : c = 1{\cdot}0772 : 1 : 1{\cdot}2402$, $\beta = 87° 1'$. When heated at 180° for 7—8 hours with a saturated alcoholic solution of ammonia, it is converted into a compound $C_{10}H_{13}NO_3$, which melts at 187°, dissolves readily in the ordinary solvents, and is isomeric with cantharidinimide.

Isocantharidin, $C_{10}H_{12}O_4$, is formed when 1 part of cantharic acid is heated with 4—5 parts of acetic chloride at 135° for three hours. It crystallises in monoclinic forms, $a : b : c = 1.0273 : 1 : 1.1795$, $\beta = 59°$; melts at 75—76°, and is readily soluble in alcohol, ether, and benzene, but only sparingly in boiling water.

Isocantharidic acid, $C_{10}H_{14}O_5 + H_2O$, is obtained by boiling the aqueous solution of isocantharidin for three hours until it no longer becomes turbid on cooling. It crystallises in crusts, loses its water of crystallisation at 100°, melts at 153°, and at 163° is converted into an anhydride which melts at 75—76°, and is reconverted into the acid by boiling with water. It is a bibasic acid. The *silver* salt, with 3 mols. H_2O, and the *barium* salt, with 5 mols. H_2O, are described; the *methyl* salt, $C_{10}H_{12}O_5Me_2$, melts at 81—82°, is volatile without decomposition, and dissolves in water and ether. W. P. W.

Gentisin. By S. v. KOSTANECKI (*Chem. Centr.*, 1891, i, 587; from *Schweiz. Wochenschr. Pharm.*, **29**, 59—60).—By boiling gentisin with hydriodic acid, methyl is eliminated with formation of *gentiseïn*, $C_{13}H_8O_5$. It crystallises in fine, straw-coloured needles with 2 mols. H_2O, which again separate at 100°, the colour deepening at the same time. By boiling with anhydrous acetic acid and anhydrous sodium acetate, *triacetylgentiseïn*, $C_{13}H_5O_5Ac_3$, is formed. It crystallises in large, lustrous needles, sparingly soluble in alcohol, readily soluble in glacial acetic acid. This compound proves the presence of three hydroxyl groups in gentiseïn, $C_{13}H_5O_2(OH)_3$, and that gentisin is a methyl ether of gentiseïn, $C_{13}H_5O_2(OMe)(OH)_2$. J. W. L.

Derivatives of Piperidine. By E. LELLMANN and R. JUST *Ber.*, **24**, 2099—2104; see also Abstr., 1887, 604; 1888, 1107; 1890, 1002).—1-*Paratolylpiperidine*, $C_6H_4Me·C_5NH_{10}$, is obtained by heating piperidine with bromotoluene for 10 hours at 270°; the portion boiling at 260—275° is separated from admixed bromotoluene by dissolving in acid, extracting with ether, and reprecipitating the base with alkali. It is a pale-yellow, oily liquid, boils at 262°, and is readily soluble in alcohol, ether, and benzene, and forms a crystalline *platinochloride*, $(C_6H_4Me·C_5NH_{10})_2,H_2PtCl_6$, which is partially decomposed on warming in aqueous solution.

1-*Parabromophenylpiperidine*, $C_6H_4Br·C_5NH_{10}$, is prepared in a similar manner from paradibromobenzene. It crystallises from ether in brownish plates, and melts at 75°. Its *hydrobromide* forms compact crystals. Hexachlorobenzene is also acted on by piperidine at 250—260°, three-fifths of the chlorine being converted into hydrochloric acid in 10 hours.

It has been shown in the previous papers that chloro- and bromonitrobenzenes of the ortho- and para-series readily combine with piperidine, whilst the meta-compounds are not acted on. This property may be employed for isolating the latter from a mixture with ortho- and para-compounds, and also for ascertaining whether such a nitro-compound is a meta-derivative or not. Thus, from the mixture obtained by nitrating parabromotoluene, the compound

$$C_6H_3Me(NO_2)Br\ [1:2:4]$$

may be readily isolated by heating with piperidine and warming the product with concentrated hydrochloric acid, which dissolves out the compound $C_6H_3Me(NO_2)\cdot C_5NH_{10}$ [1 : 3 : 4], and leaves the 1 : 2 : 4-compound as a crystalline cake. Again, the compound obtained by Fittig and Ahrens (*Annalen*, **147**, 31) by the action of nitric acid on bromometaxylene does not combine with piperidine, and, therefore, contains the nitro-group in one of the meta-positions to the bromine atoms. If the nitration be carried out with fuming nitric acid, yellow needles of *dinitrobromometaxylene*, $C_6HMe_2Br(NO_2)_2$, are obtained, which melt at 89°, and are also without action on piperidine; hence it has probably the constitution $CH_3 : NO_2 : CH_3 : Br : NO_2 = 1 : 2 : 3 : 4 : 6$.

1-*Orthamidophenylpiperidine*, $NH_2\cdot C_6H_4\cdot C_5NH_{10}$, is readily obtained by the reduction of orthonitrophenylpiperidine with stannous chloride and hydrochloric acid, and forms small plates which melt at 45·5°, and are soluble in most organic solvents. The *stannochloride*, $C_{11}H_{16}N_2,H_2SnCl_6$, crystallises in needles and melts at 217°. When the base is warmed with phenylthiocarbimide in alcoholic solution, it yields *piperidyl*-1-*thiocarbanilide*, $NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot C_5NH_{10}$, which forms white crystals, and melts at 174°. H. G. C.

Behaviour of Piperidine Bases towards Aromatic Halogen Compounds. By E. LELLMANN and R. JUST (*Ber.*, **24**, 2104—2107). —In continuation of their investigation of the action of halogen compounds on piperidine, the authors have also examined their action on the substituted piperidines. They find that the attraction between these compounds is very much less than with piperidine, and becomes smaller the nearer the alkyl group approaches the nitrogen atom, and the larger its molecular weight is. With the dipiperidyl obtained from nicotine, the reaction, as would be expected in the case of a bi-acid base, takes place rather more readily than with the alkyl derivatives.

Orthoparadinitrophenyl-α-methylpiperidine, $C_6H_3(NO_2)_2\cdot C_5NH_9Me$, is obtained from orthoparadinitrochlorobenzene and α-methylpiperidine, and forms a reddish oil, which solidifies after remaining for a long time, but could not be obtained pure. *Orthoparadinitrophenylconiine*, $C_6H_3(NO_2)_2\cdot C_5NH_9Pr^a$, forms crystals which melt at 42°, and dissolves in concentrated hydrochloric acid, alcohol, ether, and benzene. *Paranitrophenyldipiperidyl*, $NO_2\cdot C_6H_4\cdot C_5NH_9\cdot C_5NH_{10}$, is obtained as a thick, brown, aromatic-smelling oil, which did not solidify, whilst the *orthoparadinitrophenyldipiperidyl*, $C_6H_3(NO_2)_2\cdot C_5NH_9\cdot C_5NH_{10}$, forms a yellowish-red solid, without distinct crystalline form, and melts at 72—76°. It is soluble in alcohol, ether, and light petroleum and yields a sparingly soluble crystalline *platinochloride*,

$$(C_{16}H_{12}N_3O_4)_2,H_2PtCl_6.$$

The derivatives obtained from the substituted piperidines do not, therefore, show the power of crystallisation in such a marked manner as the corresponding piperidine compounds, and are, on this account, much more difficult to purify. H. G. C.

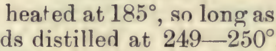
Introduction of Bivalent Radicles into Piperidine. By L. RÜGHEIMER (*Ber.*, **24**, 2186—2187).—A compound having the composition $C_{19}H_{19}N$, can be prepared by treating benzoylpiperidine with benzaldehyde and then eliminating the benzoyl group from the condensation product thus obtained; it melts at 89°, has only feeble basic properties, and is probably a dibenzenylpiperidine of the constitution $[(CHPh)_2 = 2 : 6]$. The *hydrochloride*, $C_{19}H_{19}N,HCl$, crystallises from benzene, in which it is sparingly soluble, in large plates and prisms, melts at 164·5—166°, and is decomposed by water. The *nitrate*, $C_{19}H_{19}N,HNO_3$, crystallises in colourless plates, and melts at 96·5—98°.

A crystalline base can also be obtained from the condensation product of benzoylpiperidine and cuminaldehyde in like manner, but salicylaldehyde yields an amorphous compound; aldehydes of the fatty series seem to form analogous condensation products.

F. S. K.

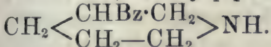
Derivatives of Homopiperidic Acid. By W. ASCHAN (*Ber.*, **24**, 2443—2450, *cf.* this vol., p. 466).—*Ethyl γ-phthalimidopropylmethylmalonate*, $C_8H_4O_2{:}N{\cdot}[CH_2]_3{\cdot}CMe(COOEt)_2$, is obtained by heating γ-bromopropylphthalimide (40 grams) for four hours in a reflux apparatus with an alcoholic solution of ethyl sodiomethylmalonate, prepared by mixing ethyl methylmalonate (28 grams) with a solution of sodium (3·7 grams) in 10 times its weight of absolute alcohol. It is an oil which could not be purified either by crystallisation or distillation.

α-Methylhomopiperidic acid, $COOH{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}NH_2$, prepared by digesting this oil with about 5·5 times its weight of hydrochloric acid (sp. gr. = 1·13) at 170—175° for four hours, crystallises in small, flat prisms or scales, melts at 168—170° with frothing, or at 157° on heating very slowly, and is readily soluble in water, but insoluble in absolute alcohol and ether. The aqueous solution is neutral to litmus, and has a pure, sweet taste. The salts with bases or acids are extremely soluble, and can be crystallised only with difficulty. The *aurochloride* is very soluble and hygroscopic; the *platinochloride*, $(C_6H_{13}O_2N)_2,H_2PtCl_6$, crystallises in thin, lustrous scales, decomposes at 190° with frothing, and is easily soluble in water, but insoluble in alcohol and ether.

β-Methylpiperidone,  $CH_2<^{CHMe\cdot CO}_{CH_2—CH_2}>NH$, is obtained when α-methylpiperidic acid is heated at 185°, so long as water distils over, and the residue is afterwards distilled at 249—250°. It crystallises from light petroleum in small, but well-formed, colourless cubes, melts at 53·5—55°, has an odour resembling that of coniine, and dissolves readily in all the ordinary solvents with the exception of cold light petroleum.

β-Ethylpiperidone is converted into an oily *nitrosamine* by the action of nitrous acid. The compound is very unstable, decomposing with the evolution of gas even at the ordinary temperature, and when heated at 115—117° until gas is no longer given off, yields α-ethyl-δ-valerolactone.

β-Propylpiperidone is gradually reconverted into α-propylhomopiperidic acid by boiling with hydrochloric acid, and on treatment with nitrous acid gives a yellow oil, having the properties of a nitrosamine.

β-Benzylpiperidone is best prepared by heating α-benzylhomopiperidic acid in quantities of 10—12 grams at 210—215° until water is no longer given off, dissolving the residue in boiling water, and allowing the hot solution to cool slowly. It is slowly reconverted into the acid by boiling with concentrated hydrochloric acid. As already stated (*loc. cit.*), it decomposes at 100°, and the products of the decomposition are now identified as nitrogen and α-benzyl-δ-valerolactone. On reduction with sodium in boiling amyl alcohol solution, β-benzylpiperidone is converted into *β-benzylpiperidine*,  $CH_2{<}\begin{matrix}CHBz\cdot CH_2\\ CH_2-CH_2\end{matrix}{>}NH$. This base is an oil of piperidine-like odour, and is characterised by forming a sparingly soluble, crystalline *platinochloride*, $(C_{12}H_{17}N)_2,H_2PtCl_6$, and an *aurochloride* which melts at 138—140°, and is readily soluble in warm water, alcohol, and ether.

Ethyl β-phthalimidoethylmalonate, $C_8H_4O_2{:}N\cdot CH_2\cdot CH_2\cdot CH(COOEt)_2$, is prepared by boiling 10 grams of β-bromethylphthalimide for four hours in a reflux apparatus with an alcoholic solution of ethyl sodiomalonate obtained from 10 grams of ethyl malonate. It crystallises from light petroleum in colourless scales or flat prisms, melts at 42—44°, is readily soluble in the ordinary solvents, and when digested with five times its weight of hydrochloric acid (sp. gr. = 1·13) at 170—180° for three hours, is converted into γ-amidobutyric acid.

W. P. W.

Substituted Ammonium Compounds. By H. Decker (*Ber.*, **24**, 1984—1987).—In addition to the methiodides described in the previous communication (this vol., p. 736), the author has endeavoured to prepare others, and finds that a number of quinoline derivatives do not combine with methyl iodide under any conditions, thus confirming the work of previous observers. The position of the substituent has a marked influence on this property, and the evidence tends to show that when a radicle is present in the position "1," a methiodide cannot be obtained; thus, 2′-nitroquinoline and 2′-nitro-3-methylquinoline, which form methiodides, no longer do so on the introduction of methyl into this position. The property is seemingly in no way dependent on the relative basicity of the quinoline derivatives, since 2′-nitro-1 : 3-dimethylquinoline forms stable salts, but no methiodide, whilst 2′-nitro-3-bromoquinoline does not give salts under the ordinary conditions, but combines with methyl iodide.

To prepare the methiodides, 3—4 hours heating at 100° with the theoretical quantity of methyl iodide is sufficient for most quinoline derivatives; a higher temperature or an excess of methyl iodide resulting frequently in the formation of insoluble compounds containing iodine. The product is extracted with ether or benzene to remove any unaltered quinoline derivative, and crystallised from water, in which the methiodides are sparingly soluble in the cold. The method can be employed to separate 1-quinoline derivatives from those which form methiodides. The preparation of methiodides is recommended as a means of characterising quinoline derivatives on account of their stability and characteristic properties, and the readiness with which they can be purified. W. P. W.

Action of Hypochlorous Acid on Bromoquinolines. By A. WELTER (*J. pr. Chem.* [2], **43**, 497—504).—The formation of carbostyril by the action of hypochlorous acid on quinoline has been investigated by Erlenmeyer and Rosenhek (Abstr., 1886, 244, 559), and by Einhorn and Lauch (Abstr., 1888, 501).

Parabromocarbostyril [Br : OH = 3 : 2′] is prepared by gradually adding a solution of 3-bromoquinoline (10 grams) in a little alcohol to a solution of boric acid (150—200 grams) in water (1½ litres) contained in a reflux apparatus, and, when it has nearly all dissolved, filtering through a hot filter into 9 litres of water; to this is added a solution of bleaching powder (1 part) in cold water (5 parts), and after 24 hours the precipitate is filtered, and dissolved in sodium hydroxide; this solution is cooled, when the *sodium* compound of parabromocarbostyril crystallises out; it is again dissolved in sodium hydroxide and decomposed by carbonic anhydride, whereby parabromocarbostyril is precipitated. It crystallises from alcohol in beautiful yellow needles, melts at 269° (uncorr.), and dissolves in alkalis, concentrated acids, chloroform, ether, and alcohol. The *potassium* and *ammonium* compounds and the *platinochloride* were obtained.

3 : 2′-*Dibromoquinoline* is obtained by heating parabromocarbostyril with excess of phosphoric bromide for two hours at 100°, decomposing the product with water, neutralising with sodium carbonate, and distilling; it crystallises in white, volatile leaflets, melts at 166—167°, and dissolves easily in alcohol and hydrochloric acid. The *platinochloride* was obtained.

Metabromocarbostyril [Br : OH = 2 : 2′] is obtained in the same way as parabromocarbostyril; it crystallises from glacial acetic acid in long, straw-like needles, and from alcohol in microscopical, four-sided tables; it sublimes unchanged in beautiful, long needles, and melts at 288°; it dissolves also in chloroform and ether. The *platinochloride* and the *sodium* and *potassium* compounds were obtained. The *compound* of it with hypochlorous acid, $C_9H_5NBrOCl$, crystallises in pale-red needles, and melts, when sharply heated, at 194°.

2 : 2′-*Dibromoquinoline* is obtained by heating metabromocarbostyril with phosphoric bromide at 130—140°, until no more hydrogen bromide is evolved, neutralising with sodium carbonate, distilling with steam, and fractionally crystallising the product from alcohol; it crystallises in colourless needles and hexagonal tables, melts at 134° (uncorr.), and dissolves in alcohol, ether, chloroform, and mineral acids; when heated with aqueous ammonia at 200°, it is converted into metabromocarbostyril. The *nitro-derivative*, $C_9H_4Br_2NO_2N$, crystallises in small, colourless needles, melts at 180°, and dissolves sparingly in hot water and ether, but easily in chloroform and concentrated mineral acids. The corresponding *amido*-derivative was obtained.

Anabromocarbostyril [Br : OH = 4 : 2′] is prepared in the same way as parabromocarbostyril; it crystallises in beautiful needles, melts at

300°, and dissolves sparingly in alcohol. The *potassium* compound is described.

4 : 2′-*Dibromoquinoline*, obtained by heating anabromocarbostyril with phosphoric bromide, crystallises in small needles, and melts at 86°.

1-Bromoquinoline yields an additive compound with hypochlorous acid (compare Einhorn and Lauch, Abstr., 1888, 502). Decker (this vol., p. 736) has investigated the action of hypochlorous acid on 4′-bromoquinoline.

Fourteen of the 21 isomeric dibromoquinolines are now known.

A. G. B.

Action of Chlorine on Hydroxyquinoline. By T. ZINCKE (*Annalen*, **264**, 196–228).—The compounds formed by the action of chlorine on parahydroxyquinoline are analogous in composition and in chemical behaviour to those produced from β-naphthol in like manner (compare Zincke and Kegel, Abstr., 1888, 708; 1889, 265); the two series of compounds are, therefore, in all probability, analogously constituted.

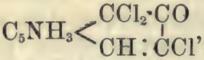
Chlorhydroxyquinoline, $C_9NH_5Cl{\cdot}OH$ [OH : Cl = 3 : 4], is deposited in the form of its hydrochloride when parahydroxyquinoline is treated with chlorine in cold glacial acetic acid solution; if the solution is saturated with chlorine and then kept for some days, tetrachloroketotetrahydroquinoline is also formed. The two products can be easily separated by treating the crystalline precipitate with water, in which the keto-derivative is insoluble; the hydrochloride of the hydroxy-compound passes into solution, and is reprecipitated on the addition of hydrochloric acid. Chlorhydroxyquinoline crystallises in long, slender, almost colourless needles, melts at 198°, and sublimes without decomposition; it is soluble in alkaline carbonates. The *hydrochloride*, C_9NH_6ClO,HCl, crystallises in yellow plates, and decomposes when heated above 200°. The *platinochloride*, $(C_9NH_6ClO)_2,H_2PtCl_6 + 2H_2O$, crystallises from hot hydrochloric acid in slender, yellow needles; the *sulphate*, $(C_9NH_6ClO)_2,H_2SO_4$, is a yellow, crystalline powder, soluble in alcohol. The *acetyl* derivative, $C_9NH_5Cl{\cdot}OAc$, crystallises from dilute alcohol in long, colourless needles, and melts at 102°.

Dichlorhydroxyquinoline, $C_9NH_4Cl_2{\cdot}OH$ [Cl_2 : OH = 2 : 4 : 3], is most easily obtained by boiling tetrachloroketotetrahydroquinoline with an aqueous solution of sodium hydrogen sulphite. It crystallises from alcohol in colourless, lustrous needles, melts at 217°, and sublimes at a higher temperature; it is readily soluble in alkaline carbonates, and, when treated with chlorine in glacial acetic acid solution, it is converted into tetrachloroketodihydroquinoline. The *hydrochloride*, $C_9NH_5Cl_2O,HCl + 2H_2O$, is a yellow, crystalline compound, and loses its water at 120—130°. The *platinochloride*,

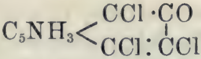
$$(C_9NH_5Cl_2O)_2,H_2PtCl_6,$$

crystallises in yellow needles, and is very sparingly soluble in water, but more readily in hot dilute hydrochloric acid. The *acetyl* derivative, $C_9NH_4Cl_2{\cdot}OAc$, separates from hot alcohol in colourless needles, and melts at 130°.

Trichlorhydroxyquinoline, $C_9NH_4Cl_3O$ [$Cl_3 : OH = 1 : 2 : 4 : 3$], is obtained when tetrachloroketodihydroquinoline is boiled with an aqueous solution of sodium hydrogen sulphite; it crystallises from hot alcohol or benzene in slender, colourless needles, melts at 244°, and is only sparingly soluble in cold alcohol; it forms stable salts with alkalis, and, when treated with chlorine in glacial acetic acid solution, it is converted into tetrachloroketodihydroquinoline. The *hydrochloride*, $C_9NH_4Cl_3O,HCl + H_2O$, crystallises from hot hydrochloric acid in lemon-yellow needles, and is decomposed by warm water; the platinochloride forms brownish-yellow needles. The *acetyl* derivative, $C_9NH_3Cl_3{\cdot}OAc$, crystallises from hot alcohol in slender, colourless needles, sinters together at 130°, and melts at 139°.

Trichloroketodihydroquinoline,  $C_5NH_3<\begin{matrix}CCl_2{\cdot}CO\\ \vert\\ CH:CCl\end{matrix}$, is formed with elimination of 1 mol. HCl when tetrachloroketotetrahydroquinoline is slowly heated to 100° with water; it separates from a mixture of ether and light petroleum in transparent, well-defined, seemingly monoclinic crystals, melts at 105—106°, and is readily soluble in hot alcohol, chloroform, and carbon bisulphide; it seems to form a hydrate with water, and it dissolves in alkalis yielding a brownish solution, from which the hydrochloride of dichlorhydroxyquinoline is precipitated on the addition of hydrochloric acid. When heated with an aqueous solution of sodium hydrogen sulphite, and when boiled for a long time with water or dilute acids, it is converted into dichlorhydroxyquinoline. The *hydrochloride*, $C_9NH_4Cl_3O,HCl$, prepared by passing hydrogen chloride into a chloroform solution of the base, crystallises in small needles, and decomposes on exposure to the air.

Anilidodichlorhydroxyquinoline, $C_{15}N_2H_{10}Cl_2O$ [$NHPh : Cl_2 : OH = 1 : 2 : 4 : 3$], is deposited in red needles when aniline is added to a cold alcoholic solution of trichloroketodihydroquinoline; after keeping for 12 hours, the solution is acidified with dilute acetic acid, the insoluble residue dissolved in hot alcohol, reprecipitated from the solution with hydrochloric acid, and the hydrochloride obtained in this way decomposed with sodium acetate. The base exists in two forms, both of which melt at 154°; when it is dissolved in hot dilute alcohol, and the solution then allowed to cool, long, colourless needles are deposited, but after some time dark-orange, cubic crystals separate from the solution, and finally the colourless needles undergo transformation into the dark crystals; if the latter are again dissolved in alcohol, the same phenomena are observed. Both modifications are readily soluble in alcohol, glacial acetic acid, and benzene, but more sparingly in light petroleum; they dissolve in alkalis yielding an almost colourless solution, in which a heavy, white precipitate is produced on the addition of acetic acid; this precipitate gradually changes to a mass of small, orange crystals. The *hydrochloride*, $C_{15}N_2H_{10}Cl_2O,HCl$, crystallises in brownish, lustrous prisms; the platinochloride is decomposed by hot water. The *acetyl* derivative, $C_{15}N_2H_9Cl_2{\cdot}OAc$, crystallises from hot alcohol in yellow plates, melts at 170°, and is sparingly soluble in cold alcohol.

Tetrachloroketodihydroquinoline,  $C_5NH_3<\begin{matrix}CCl\cdot CO\\ \qquad\ \ \vert\\ CCl:CCl\end{matrix}$, can be obtained by treating dichlorhydroxy- or trichloroketodihydro-quinoline with chlorine in glacial acetic acid solution; the product is purified by recrystallisation from boiling light petroleum, from which it is deposited on cooling in light-yellow, well-defined plates melting at 82—83°. It is readily soluble in ether, chloroform, benzene, glacial acetic acid, hot light petroleum, and hot alcohol, and it dissolves in alkalis yielding a brown solution, which quickly changes, first to green, and then to deep blue; it is gradually converted into trichlorhydroxyquinoline on prolonged boiling with dilute alcohol or dilute acids. The *hydrochloride*, $C_9NH_3Cl_4O,HCl$, is crystalline, and decomposes on exposure to the air, with liberation of hydrogen chloride.

Anilidotrichloroketodihydroquinoline,

$$C_{15}N_2H_9Cl_3O\ [NHPh : Cl : O : Cl_2 = 1 : 2 : 3 : 4],$$

is gradually deposited when excess of aniline is added to a solution of tetrachloroketodihydroquinoline in cold alcohol; it crystallises from glacial acetic acid in brownish-yellow prisms, melts at 200—202° with decomposition, and is only sparingly soluble in alcohol and glacial acetic acid, and insoluble in soda. When treated with stannous chloride in glacial acetic acid solution, it is converted into the anilide of dichlorhydroxyquinoline (see above).

Chloranilidoquinolinequinoneanilide,

$$C_{21}N_3H_{14}ClO\ [NPh : Cl : NHPh : O = 1 : 2 : 3 : 4],$$

is formed when the preceding compound is boiled with aniline in alcoholic solution or treated with aniline at the ordinary temperature; it crystallises from alcohol and glacial acetic acid in dark, ruby-red plates or needles, melts at 180° with decomposition, and is only sparingly soluble in alcohol, but more readily in glacial acetic acid and benzene. The hydrochloride crystallises in brownish, lustrous plates, and is decomposed by water.

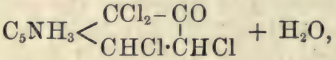
Chlorhydroxyquinolinequinoneanilide,

$$C_{15}N_2H_9ClO_2\ [NPh : Cl : OH : O = 1 : 2 : 3 : 4],$$

is precipitated when the preceding compound is boiled with 10 per cent. soda and a little alcohol, until it has completely dissolved, and the solution then acidified with acetic acid. It crystallises from hot alcohol in deep-red plates or needles, melts at 195°, and is readily soluble in glacial acetic acid and hot alcohol; it dissolves in soda with a brownish-red coloration, but it is insoluble in sodium carbonate.

Chlorhydroxyquinolinequinone, $C_9NH_4ClO_3$ $[O_2 : Cl : OH = 1 : 4 : 2 : 3]$, can be obtained by boiling chloranilido- or chlorhydroxyquinolinequinoneanilide with alcoholic hydrochloric acid, decomposing the hydrochloride produced in this way with sodium carbonate, and then precipitating the product with acetic acid. It crystallises in dark, reddish-brown needles, melts at about 280° with decomposition, and is readily soluble in sodium carbonate, but only sparingly in the ordinary organic solvents. The hydrochloride crystallises in yellowish, lustrous plates.

Tetrachloroketotetrahydroquinoline hydrate,



$$C_5NH_3<\begin{array}{l}CCl_2-CO\\ CHCl\cdot CHCl\end{array} + H_2O,$$

is the final product of the action of chlorine on a glacial acetic acid solution of parahydroxyquinoline. It is a light-yellow, granular, crystalline powder, which turns brown at about 180°, and melts at 200° with decomposition; it is sparingly soluble in the ordinary solvents, cannot be purified by recrystallisation, and when heated with water, it is converted into dichlorhydroxyquinoline.

F. S. K.

Halogen Alkyl Compounds of Parahydroxyquinoline and the Derived Quaternary Ammonium Bases. By A. Claus and H. Howitz (*J. pr. Chem.*, [2], **43**, 505—530).—The authors have already shown (Abstr., 1890, 1323) that the action of alkalis on the halogen alkyl compounds of orthohydroxyquinoline differs from that of the same reagents on parahydroxyquinoline; in the latter case, bases are produced which possess all the characteristic properties of quaternary ammonium bases. It is also found that alkalis and moist silver oxide produce the same bases when they act respectively on parahydroxyquinoline, but different bases when they act on para-alkyloxyquinoline. The first portion of this paper is devoted to the authors' explanation of these phenomena, involving some remarks on the constitution of quinoline and isoquinoline; for the appreciation of these the original must be consulted.

Parahydroxyquinoline methochloride [OH : MeCl = 3 : 1′] (*loc. cit.*) loses 1 mol. H_2O at 100°, becoming porcelain-like, but retaining its crystalline form; it darkens at 250°, and at 270—275° it froths up and decomposes. The *platinochloride* decomposes at 255°.

Parahydroxyquinoline methosulphate, $(C_9NH_6\cdot OH)_2Me_2SO_4$, obtained by double decomposition from the methiodide and silver sulphate, crystallises from aqueous alcohol in slender, yellowish needles, with 5 mols. H_2O, which are lost at 110°.

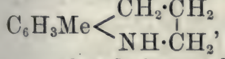
Parahydroxyquinoline methohydroxide, $C_9NH_6\cdot OH,MeOH$, is obtained by the action of alkalis, ammonia, or moist silver oxide on the methyl halogen compounds, or by decomposing the methosulphate with barium hydroxide. It is very soluble in water, yielding a yellow solution, from which it crystallises only after prolonged exposure over sulphuric acid, when it forms bright-yellow, flat needles (with 1 mol. H_2O); it dissolves freely in hot alcohol to a reddish solution, from which it crystallises on cooling in beautiful, yellow prisms (with 1 mol. H_2O); both solutions are strongly alkaline. It is quite insoluble in ether, which precipitates it in yellow needles from alcohol; hot chloroform dissolves it slightly with a violet colour. It loses its water of crystallisation at 100—110°, becoming nearly black, but it does not fully decompose until 200°. Hydrochloric acid converts it into the methochloride. When it is exposed over sulphuric acid for 14 days, it loses 2 mols. H_2O, becoming *parahydroxyquinolinemethyl-*

betaïne, C_9NH_6MeO; this retains the crystalline form of the methohydroxide, but is dark red and opaque; it is very hygroscopic, recombining with water to form the methohydroxide. The methohydroxide absorbs carbonic anhydride both in aqueous and alcoholic solution very readily, the solution becoming brighter in colour and less alkaline, but the carbonate which is probably formed could not be isolated; the addition of ether to the solution precipitates only the methohydroxide.

Parahydroxyquinoline ethobromide, $C_9NH_6{\cdot}OH,EtBr$, is easily obtained by heating the components for several hours in a closed vessel on the water-bath; it crystallises in large, brilliant, vitreous, anhydrous tables and columns, decomposes at 240—245°, and dissolves easily in alcohol and water.

Parahydroxyquinoline ethohydroxide crystallises in amber-red, vitreous prisms and columns (with 1 mol. H_2O); it is very similar in properties to the methohydroxide, but is somewhat more soluble in hot chloroform and less stable, decomposing at 140°.

Parahydroxyquinoline benzychloride, $C_9NH_6{\cdot}OH,C_7H_7Cl$, obtained by heating a mixture of benzyl chloride with parahydroxyquinoline in molecular proportion on the water-bath, crystallises in massive, colourless tables (with $1\frac{1}{2}$ mols. H_2O); if a hot concentrated solution of it is rapidly cooled, it separates as a yellowish oil which crystallises with difficulty; it loses its water of crystallisation at 100° and melts with decomposition at 235—237°. The *platinochloride* is described. The *benzyhydroxide*, prepared like the methohydroxide, crystallises from a hot aqueous solution in brilliant, red, long columns or short prisms (with 2 mols. H_2O) of the colour of potassium dichromate; it is sparingly soluble in cold water, but easily soluble in hot water and alcohol to reddish-yellow, strongly alkaline solutions; it is insoluble in ether, but sparingly soluble in chloroform, which, however, will not extract it from its aqueous solution; it melts in its water of crystallisation at 100°, and decomposes at 120—125°. When the crystallised benzyhydroxide is exposed over sulphuric acid for some 13 days, it loses 3 mols. H_2O, being converted into the *anhydride*, $C_9NH_6{\cdot}O{\cdot}CH_2Ph$, which is a dark-red, very hygroscopic powder; water reconverts it into the hydroxide. A. G. B.

Homologues of Tetrahydroquinoline. By E. BAMBERGER and P. WULZ (*Ber.*, **24**, 2055—2076).—*Tetrahydro*-1-*methylquinoline*,  $C_6H_3Me{<}\begin{matrix}CH_2{\cdot}CH_2\\ |\\ NH{\cdot}CH_2\end{matrix}$, is obtained by reducing 1-methylquinoline with granulated tin and hydrochloric acid, decomposing the stannochloride with aqueous soda, distilling in a current of steam, and extracting the distillate with ether. It is a colourless oil which has a penetrating odour, boils at 255—257° under 717 mm. pressure, and quickly assumes a yellow colour in the air. Its *hydrochloride*, $C_{10}H_{13}N,HCl$, forms monosymmetric tablets, and is readily soluble in water, hot chloroform, and alcohol, but insoluble in benzene, ether, and light petroleum. Its acid solution becomes brownish-yellow on the addition of potassium dichromate, and afterwards assumes a dark, brownish-green colour. The *acetyl* compound, $C_{10}H_{12}NAc$, forms vitreous prisms, melts at 53—54°, and boils at 297—299° under a pressure of 718 mm., and the *nitroso*-compound, $C_{10}H_{12}N{\cdot}NO$, which separates from dry ethereal solution in thin, almost colourless, six-sided plates, and from alcohol in monosymmetric crystals, is readily soluble in organic solvents, and melts at 51°.

Tetrahydro-1-methylquinoline also combines with diazobenzene chloride if all mineral acids be removed by the addition of sodium acetate, forming the *diazoamido*-compound, $C_{10}H_{12}N{\cdot}N_2Ph$, which crystallises in slender, yellow needles, and shows all the characteristic reactions of benzene diazoamido-compounds. It is at once converted in alcoholic solution by a trace of mineral acid into the isomeric azo-colouring matter.

Tetrahydro-1-*methylquinoline*-3-*azobenzenesulphonic acid*,

$$C_9NH_9Me{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H,$$

is obtained by the action of paradiazobenzenesulphonic acid on the hydrochloride of the base suspended in water. The liquid, as in the case of tetrahydroquinoline, at once assumes a red colour, and in a short time deposits small, brownish-violet needles. It is sparingly soluble in boiling water, readily in alkalis, and is precipitated from the latter solutions, on the addition of hydrochloric acid, in feathery aggregates of dark-violet needles. It colours wool and silk orange-yellow in an acid-bath, and shows the bad tinctorial properties of the tropæolines in a marked degree. Its *sodium* salt forms brick-red flakes, which gradually change to thin, lustrous plates with a green surface lustre.

The azo-colour is converted into the corresponding *tetrahydro*-1-*methyl*-3 *amidoquinoline*, $C_9NH_9Me{\cdot}NH_2$, by treatment with tin and hydrochloric acid; the stannochloride first formed is decomposed by aqueous soda, the base extracted with ether, and converted into the *hydrochloride*, which is purified by dissolving in alcohol and a little water, adding ether till turbidity commences, and allowing to crystallise; it then forms monosymmetric tablets ($a:b:c = 2{\cdot}3876:1:0{\cdot}8830$, $\beta = 77°\ 46{\cdot}9'$). It does not melt at 310°. The base shows all the properties of a paradiamidobenzene, giving the various colouring matters, such as thionins, indamins, safranins, &c., characteristic for this class of compounds.

Tetrahydro-3-*methylquinoline*, $C_9NH_{10}Me$, is obtained from 3-methylquinoline in the manner already described. It forms silver-white prisms, melts at 38°, boils at 262·3° under a pressure of 712 mm., and is readily soluble in organic solvents, very slightly in water. The *hydrochloride*, $C_{10}NH_{13},HCl$, crystallises in large, silky needles or vitreous prisms, melts at 189°, and is readily soluble in alcohol and water, insoluble in ether, light petroleum, and benzene. Its neutral solution gives a reddish-brown coloration with ferric chloride, which finally becomes olive-green. The *acetyl* compound, $C_{10}NH_{12}Ac$, is a thick, colourless oil and boils at 302—305° under a pressure of 719 mm.; the *nitroso*-compound, $C_{10}NH_{12}{\cdot}NO$, forms long, straw-yellow, flat prisms, belonging to the monosymmetric system, melts at 65°, and gives Liebermann's reaction. The *diazoamido*-compound, $C_{10}NH_{12}{\cdot}N_2Ph$, crystallises in beautiful, satiny prisms, melts at 74·5°, and does not yield the isomeric compound even on boiling with acids, but is simply converted into phenol and tetrahydro-3-methylquinoline, according to the characteristic reaction for diazoamido-compounds, in which the hydrogen atom in the para-position is displaced, as, for example, in methylparatoluidine (this vol., p. 1202). In other respects this compound shows the reactions of a diazoamido-compound.

Tetrahydro-3-methylquinoline-1-azobenzenesulphonic acid,

$$C_9NH_9Me\cdot N_2\cdot C_6H_4\cdot SO_3H,$$

is formed by the action of paradiazobenzenesulphonic acid on tetrahydro-3-methylquinoline, but the reaction takes place much less readily and with a smaller yield than in the case of the 1-methyl compound, which is characteristic of compounds in which the para-position to the amido-group is occupied. The colouring matter is a dark-violet, crystalline powder, and dissolves in alcohol and to a smaller extent in water, forming a wine-red solution, which changes to violet on the addition of mineral acids. Its *sodium* salt forms claret-coloured needles, with a brownish-green metallic lustre. The colouring matter dyes wool and silk red in an acid-bath.

1-*Amidotetrahydro-3-methylquinoline*, $C_9NH_9Me\cdot NH_2$, is formed by the reduction of the azo-colour with zinc-dust and soda solution. Its *hydrochloride* forms colourless prisms with a vitreous lustre and melts at 216°. Its neutral solution gives, with oxidising agents, the bordeaux-red coloration so characteristic of orthodiamido-compounds, and it also behaves towards hydroxynaphthoquinone like other alkylated orthodiamidobenzenes, forming a rosindone (this vol., p. 746). It further resembles these compounds inasmuch as it is acted on by acetic acid with formation of an anhydro-base or *imidazole*, $C_9H_9Me{<}\genfrac{}{}{0pt}{}{N}{N}{>}CMe$, which crystallises from light petroleum in long, white needles or small, flat, lustrous prisms, melts at 163°, distils unchanged at about 360°, and sublimes in beautiful needles. Its *picrate* forms a sandy, yellow, crystalline powder, and the *chromate* fascicular aggregates of yellow needles. When heated with phthalic anhydride, it yields the *phthalone*, $C_{12}H_{11}N_2\cdot CH\colon C_2O_2\colon C_6H_4$, which crystallises from acetic acid in slender, golden-yellow prisms with a silky lustre, and does not melt at 310°.

Sulphobenzenediazoamidotetrahydro-3-methylquinoline,

$$C_{10}NH_{12}\cdot N_2\cdot C_6H_4\cdot SO_3H,$$

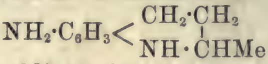
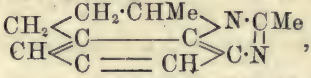
is always formed together with the azo-colour above described, in spite of the presence of a large excess of mineral acid, which again forms a striking example of the similarity between the hydroquinoline and methylparatoluidine (this vol., p. 1202). The compound is isolated as the *sodium* salt, which has a pure white colour, and explodes on heating; the *barium* salt forms white, glistening plates.

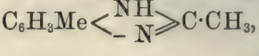
Tetrahydro-1 : 3-*dimethylquinoline*, $C_9NH_8Me_2$, is obtained by the reduction of 1 : 3-dimethylquinoline in the usual manner, and is a colourless oil boiling at 272—273° under a pressure of 720 mm. The *hydrochloride*, $C_{11}NH_{15},HCl$, crystallises in rhombic prisms ($a : b : c$

= 0·6694 : 1 : 1·0880), and melts at 212° ; in neutral solution it gives with ferric chloride a yellowish-green coloration, which gradually changes to emerald-green, and, on warming, becomes yellowish-brown. The *acetyl* compound is a thick, colourless oil boiling at 313·5° under a pressure of 719 mm., and the *nitroso*-compound, $C_{11}NH_{14}\cdot NO$, crystallises from alcohol on addition of water in thin, lustrous, polygonal plates, melts at 42°, and gives Liebermann's reaction. The *diazoamido*-compound, $C_{11}NH_{14}\cdot N_2Ph$, forms thin, strongly lustrous prisms, melts at 88—89°, and undergoes no molecular change with mineral acids, but is simply converted into phenol and tetrahydro-1 : 3-dimethylquinoline.

The above results show that tetrahydro-1-methylquinoline, tetrahydro-3-methylquinoline, and tetrahydro-1 : 3-dimethylquinoline correspond exactly in their properties with methylorthotoluidide, methylparatoluidine, and asymmetrical methylxylidine respectively, and form, therefore, additional evidence in favour of Bamberger's theory that the tetrahydroquinolines have no longer any specific quinoline properties, but behave simply as substituted amidobenzenes (Abstr., 1890, 1301). H. G. C.

Tetrahydro-1-amidoquinaldine. By E. BAMBERGER and P. WULZ (*Ber.*, **24**, 2049—2055).—According to Bamberger's theory (Abstr., 1890, 1301) the tetrahydro-derivatives of 1-amidoquinolines should behave in all respects as alkyl-substituted orthodiamidobenzenes. To test the truth of this supposition, the authors have prepared tetrahydro-orthamidoquinaldine and examined its properties, which they find to agree exactly with the demands of the theory.

Tetrahydro-1-*amidoquinaldine*,  $NH_2\cdot C_6H_3<\begin{matrix}CH_2\cdot CH_2\\ NH\cdot CHMe\end{matrix}$, is readily formed by boiling orthamidoquinaldine with tin and hydrochloric acid, collecting the stannochloride, triturating it with aqueous soda until it forms an emulsion, and extracting the latter with chloroform. It gives the red coloration characteristic of orthodiamido-compounds with ferric chloride and potassium dichromate, and, on boiling with acetic acid, acetic anhydride, and sodium acetate, yields an anhydrobase, or imidazole, according to Hantzsch's nomenclature, which has the constitution  $\begin{matrix}CH_2<\begin{matrix}CH_2\cdot CHMe\\ C\text{———}C\end{matrix}>N\cdot CMe\\ CH\ll C = CH\gg C\cdot N\end{matrix}$, and is termed by the authors "*α-methyltetrahydroperichinaldimidazole.*" When crystallised slowly from ether, it forms acute, flat prisms, having an adamantine lustre, and melts at 110° ; it possesses all the usual characteristics of an imidazole, is an extremely stable base, readily soluble in acids, and does not give the least coloration with oxidising agents. Its *platinochloride* forms lustrous, orange-red prisms, and may be crystallised without decomposition from boiling water.

In the methylated imidazoles of the benzene series, the methyl group, like that in quinaldine, readily undergoes condensation. For example, Bamberger and Berlé will shortly publish a paper showing that the imidazole 1 : 3 : 4-diamidotoluene,  $C_6H_3Me<\begin{matrix}NH\\ N\end{matrix}\gg C\cdot CH_3$, readily combines with phthalic anhydride, forming the *phthalone*, $C_6H_3Me<\substack{NH\\-N}\geqslant C\cdot CH{:}C_2O_2{:}C_6H_4$. The above imidazole in like manner combines with phthalic anhydride, forming a phthalone of the formula $C_9H_8Me\leqslant\substack{N\\N}\geqslant C\cdot CH{:}C_2O_2{:}C_6H_4$, which separates from acetic acid on the addition of water in indistinct, yellow crystals, and sublimes in slender, lustrous needles. That the condensation has not taken place between the methyl group of the reduced pyridine ring is shown by the fact that α-tetrahydroquinaldine itself does not form a phthalone with phthalic anhydride.

The paper also contains a reply to certain criticisms of Hinsberg (this vol., p. 393) with regard to the centric formula proposed by Bamberger for piaselenols. H. G. C.

Derivatives of 1-Methylquinoline and 3-Methylquinoline. By E. Lellmann and H. Ziemssen (*Ber.*, **24**, 2116—2120).—3-*Nitro*-1-*methylquinoline*, $C_9NH_5Me\cdot NO_2$, is prepared by means of Skraup's reaction from nitro-orthotoluidine, and forms delicate crystalline nodules, melts at 129°, and is scarcely soluble in water, but readily in alcohol The *hydrochloride*, $C_{10}H_8N_2O_2,HCl + H_2O$, crystallises in white nodules, and the *platinochloride*, $(C_{10}H_8N_2O_2)_2,H_2PtCl_6$, in beautiful rhombic crystals. 1-*Methylquinolinesulphonic acid*, $C_9NH_5Me\cdot SO_3H$, is obtained by the action of fuming sulphuric acid, containing 1 part of anhydride in 3 parts of acid, on 1-methylquinoline, and is isolated by means of its barium salt; it crystallises from water in concentric aggregates of slender needles, is sparingly soluble in cold, more readily in hot water, but insoluble in alcohol; and on heating blackens without melting. The *nickel* salt,

$$(C_{10}NH_8\cdot SO_3)_2Ni + 7\tfrac{1}{2}H_2O,$$

forms green, six-sided plates. When treated with tin and hydrochloric acid on the water-bath, it yields *tetrahydro*-1-*methylquinolinesulphonic acid*, $C_9NH_9Me\cdot SO_3H$, which crystallises in colourless plates.

3-*Methylquinolinesulphonic acid*, $C_9NH_5Me\cdot SO_3H$, is obtained in the same manner as the 1-methyl compound, and forms yellowish crystals, does not melt or decompose at 280°, and is very slightly soluble in water, and insoluble in alcohol. The *zinc* salt, $(C_{10}NH_8\cdot SO_3)_2Zn + 4H_2O$, forms white, crystalline nodules, and the *silver* salt a white, voluminous precipitate. On reduction, it yields *tetrahydro*-3-*methylquinolinesulphonic acid*, $C_9NH_9Me\cdot SO_3H + 2H_2O$, which crystallises from water in silky needles.

The 1-methylquinoline-3-sulphonic acid obtained by Herzfeld (Abstr., 1884, 1199) from orthotoluidinesulphonic acid requires nearly 500 parts of water at 18·8° for its solution, and forms a *barium* salt $(C_{10}NH_8\cdot SO_3)_2Ba + 5H_2O$, crystallising in white, asbestos-like aggregates of needles. On reduction, it is converted into *tetrahydro*-1-*methylquinoline*-3-*sulphonic acid*, $C_9NH_9Me\cdot SO_3H$, which forms colourless crystals, and, in aqueous solution, gives, with potassium dichromate, a brown, and with ferric chloride, a green coloration.

H. G. C.

Constitution of Phenanthroline Bases. By H. SCHIFF (*Ber.*, **24**, 2127—2130).—This paper is a reply to the criticisms of v. Miller (this vol., p. 1103) on the constitutional formulæ put forward by the author and Vanni (Abstr., 1890, 138) for the phenanthroline derivatives; the author accepts the formulæ assigned by Miller to the compounds in question, but thinks that Miller has gone a little too far in stigmatising the whole of his (the author's) experimental work as incorrect. F. S. K.

Reduction of Tricyclic Systems. By E. BAMBERGER (*Ber.*, **24**, 2463—2469).—As the two best known tricyclic compounds, anthracene and phenanthrene, take up only 2 and 4 atoms of hydrogen respectively on reduction, attention has been directed to the effect of reduction on the naphthaquinolines, and the results obtained with α-naphthaquinoline are given in the two following abstracts. The reduction of bicyclic compounds is, in all respects, comparable with that of tricyclic compounds (see Abstr., 1890, 1299), and proceeds in two well-defined stages, a tetrahydro-derivative being formed with tin and hydrochloric acid, and an octohydro-derivative with sodium and amyl alcohol as reducing agents. In every case, 4 hydrogen atoms are taken up in the first instance by the "pyridine ring," and the resulting tetrahydronaphthaquinolines resemble the alkylated naphthylamines in properties. The further addition of 4 hydrogen atoms leads to the reduction of one or other of the two nitrogen-free rings with the production of octohydro-derivatives, having the properties of "alicyclic" or "aromatic" alkylated tetrahydro-naphthylamines as the case may be. α-Naphthaquinoline gives only the "aromatic" octohydro-derivative on reduction. The remainder of the paper is devoted to a restatement of the effect of reduction on the properties of the naphthaquinolines, for which a previous paper (Abstr., 1890, 1303) may be consulted. W. P. W.

Tetrahydro-α-naphthaquinoline. By E. BAMBERGER and L. STETTENHEIMER (*Ber.*, **24**, 2472—2480).—α-Naphthaquinoline is best prepared by heating α-naphthylamine (100 grams), nitrobenzene (46 grams), glycerol (178 grams), and concentrated sulphuric acid (141 grams) for five hours, or longer, at 160°, stirring the product into four times its volume of water, adding a concentrated solution of caustic potash (65—70 grams), filtering from the separated resin and potassium sulphate, rendering strongly alkaline with aqueous caustic soda, and extracting with ether. After removal of the ether by evaporation, the oily residue is dissolved in sulphuric acid (55 grams) diluted with about 13 times its weight of water, and purified by adding concentrated aqueous potassium dichromate to the boiling solution until no further separation occurs and the solution becomes green, filtering, rendering alkaline with caustic soda, and extracting with ether. It crystallises from light petroleum in colourless, thick, monoclinic tables, melts at 52°, boils at 223° under 47 mm., at 338° under 719 mm. pressure (not at 251° under 747 mm. pressure, as stated by Skraup), and has only a very slight odour unlike that of quinoline. On treatment in concentrated hydrochloric solution with ferric chloride, it yields a compound which crystallises from alcohol in golden-yellow, silky needles, and dissolves readily in water, but only sparingly in hydrochloric acid.

Tetrahydro-α-naphthaquinoline, $C_{13}H_{12}\!:\!NH$, is obtained when α-naphthaquinoline (20 grams), dissolved in hydrochloric acid, is gradually added to a boiling mixture of tin (80 grams) and 38 per cent. hydrochloric acid (500 grams), and heated until the metal is dissolved. The yield amounts to 13—14 grams of the tetrahydro-derivative with the quantities given, and, in addition, a base of high melting point is formed, which can readily be separated from the chief product, as it dissolves only sparingly in ether and light petroleum. Tetrahydro-α-naphthaquinoline crystallises from light petroleum in snow-white, strongly-lustrous scales, melts at 46°, and dissolves readily in the ordinary solvents. The solutions exhibit a marked blue fluorescence, which disappears, however, on the addition of a trace of an alkali or mineral acid. Oxidising agents, added to the acid solution, produce an intense carmine colour, and when the solution to which potassium dichromate has been added is allowed to remain for a few minutes, the chromate of a new base separates in dark-green needles, resembling quinhydrone in appearance. The *acetyl* derivative is a viscid oil. The *hydrochloride*, $C_{13}NH_{13},HCl$, crystallises in thick prisms, melts at 260—261°, is tolerably soluble in water, sparingly soluble in hydrochloric acid, and, when evaporated with hydrochloric acid, is converted into a new (? polymeric) base which crystallises in lustrous needles, does not melt at 270°, and is very sparingly soluble in ether and light petroleum (*v. supra*). The *nitroso*-derivative, $C_{13}NH_{12}\cdot NO$, crystallises from light petroleum in flat, broad, lemon-yellow prisms, melts at 59·5°, and is very soluble in the ordinary solvents, water excepted.

Phenylazotetrahydro-α-naphthaquinoline crystallises from dilute alcohol in groups of cherry-red needles which exhibit a strong bronze lustre, dissolve in the ordinary solvents with a deep orange-red colour, and in concentrated sulphuric acid with a cornflower-blue colour. The *sulphate*, $(C_{13}H_{11}NH\cdot N_2Ph)_2,H_2SO_4$, crystallises in olive-green, flat prisms, and yields violet-red solutions. *Sulphophenylazotetrahydro-α-naphthaquinoline*, $C_{13}H_{11}NH\cdot N_2\cdot C_6H_4\cdot SO_3H$, is a dark violet-red, crystalline powder, and its *sodium* salt an orange-red, crystalline precipitate.

Paramidotetrahydro-α-naphthaquinoline, obtained by reduction of the phenylazo-derivative with stannous chloride and hydrochloric acid, dissolves readily in alcohol and ether, and is very unstable. The *hydrochloride*, $C_{13}H_{14}N_2,2HCl$, crystallises in small, white needles, does not melt at 300°, and dissolves readily in water and dilute alcohol, but very sparingly in strong hydrochloric acid. On treatment with hydrochloric acid, hydrogen sulphide, and ferric chloride, it gives a brownish-red coloration; with aniline, potassium dichromate, and acetic acid, a brownish-red colour which on boiling becomes dark-claret, with α-naphthol in alkaline solution a greenish-blue, flocculent precipitate, and with bleaching powder a chlorimide which dissolves readily in alcohol and ether. When the hydrochloride is fused with a mixture of aniline hydrochloride with some aniline and amidoazobenzene for some minutes, a deep violet-red melt is obtained, which, in alcoholic solution, has a beautiful violet colour, and exhibits an intense reddish-violet fluorescence. The production, under these conditions, of colouring matters which form fluorescent alcoholic solutions serves to distinguish paradiamines of the naphthalene series from those of the benzene series. W. P. W.

"Aromatic" Octohydro-α-naphthaquinoline. By E. BAMBERGER and L. STEITENHEIMER (*Ber.*, **24**, 2481—2495).—*ar.-Octohydro-α-naphthaquinoline*,* $C_{13}H_{16}\colon NH$, is prepared by reducing α-naphthaquinoline dissolved in 20 times its weight of amyl alcohol with 2·5 times its weight of sodium, shaking the product with an equal volume of water, treating the upper layer with hydrochloric acid, removing the amyl alcohol by steam distillation, extracting the residue with ether to remove impurities, adding caustic soda to alkaline reaction, and purifying the liberated base by steam distillation or extraction with ether. The yield amounts to at least 60 per cent. of the α-naphthaquinoline reduced. It crystallises in thick, colourless rhombohedra, melts at 47—48°, boils at 216° under 37·5 mm. pressure, is only slightly volatile with steam, has a peculiar, sweet odour, and dissolves readily in all ordinary solvents, except water. Like the "aromatic" tetrahydronaphthylamines, it reduces silver nitrate in alcoholic solution; with ferric chloride in acid solution, it gives, on warming, a beautiful carmine colour, which disappears on cooling, with potassium dichromate, a carmine colour, either on warming or after remaining for a short time in the cold, and with chromic acid, a fleeting, deep violet-red colour. The *hydrochloride*, $C_{13}NH_{17},HCl$, crystallises in monoclinic tables, $a : b : c = 1{\cdot}0789 : 1 : 1{\cdot}7101$, $\beta = 68° 7'$; forms observed $\infty\bar{P}\infty$, ∞P, P, $\frac{1}{2}\bar{P}\infty$, and $\not{P}\infty$, and dissolves very readily in water, but only sparingly in hydrochloric acid; the *hydrogen sulphate* $C_{13}NH_{17},H_2SO_4$, crystallises from ether-alcohol in stellate groups of needles, melts at 187°, and is extremely soluble in water; the *picrate*, $C_{13}NH_{17},C_6H_2(NO_2)_3{\cdot}OH$, melts at 155—156°, and is tolerably soluble in hot water; the *platinochloride*, $(C_{13}NH_{17})_2,H_2PtCl_6$, is a crystalline powder, which, by varying the conditions of preparation, seems to exist in three forms of different colours and degrees of hydration.

The *nitroso*-derivative, $C_{13}NH_{16}{\cdot}NO$, crystallises from alcohol in small, yellowish rosettes, and melts at 77·5°. The *acetyl* derivative, $C_{13}H_{16}\colon NAc$, crystallises from light petroleum in colourless, lustrous, triclinic prisms, melts at 68—69°, and dissolves sparingly in water but readily in the ordinary solvents. The *methyl* derivative, $C_{13}H_{16}\colon NMe$, crystallises from alcohol in large, thin, nacreous scales, and melts at 37—38°; its *hydriodide*, $C_{13}H_{16}\colon NMe,HI$, crystallises from hot water in long, lustrous, silky needles, and melts at 202°, and its *platinochloride* is a yellow, crystalline precipitate.

Sulphophenylazo-ar.-octohydro-α-naphthaquinoline,

$$C_{13}NH_{16}{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H,$$

crystallises in slender, violet-brown, lustrous needles, is sparingly soluble in alcohol and water, dissolves in concentrated sulphuric acid with a deep-violet colour, and, in an acid-bath, dyes wool and silk a bright red. *Phenylazo-ar.-octohydro-α-naphthaquinoline* is obtained as sulphate when the reddish-yellow (? diazoamido-) compound resulting from the action of diazobenzene chloride on octohydro-α-naphthaquinoline in the presence of excess of sodium acetate is warmed with dilute sulphuric acid. It crystallises in lustrous, orange-red prisms, melts at 118·5°, and is very sparingly soluble in alcohol. Its *sulphate* crystallises from alcohol in beautiful cherry-red prisms with a bronze lustre, melts at 190·5° and dissolves in concentrated sulphuric acid with an olive-green colour.

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* For nomenclature, compare Abstr., 1890, 1303.

ar.-Octohydroparamido-α-naphthaquinoline, $NH_2\cdot C_{13}H_{15}\vdots NH$, obtained by the reduction of phenylazo-ar.-octohydro-α-naphthaquinoline with stannous chloride in hydrochloric acid solution, forms tufts of lustrous, flat, white prisms, melts at 97°, is not affected by exposure to light and air, and dissolves very readily in chloroform and alcohol, easily in ether, but only sparingly in water or cold light petroleum. The *hydrochloride* is very soluble in water, and crystallises in lustrous, white needles. With hydrochloric acid, hydrogen sulphide, and ferric chloride, the aqueous solution of the salt gives a thionine of a beautiful crimson colour; with metatolylenediamine hydrochloride and sodium acetate, it yields colouring matters of the tolylene-blue and tolylene-red series; with α-naphthol in alkaline solution, it forms a beautiful greenish-blue dye of the indophenol class; with aniline hydrochloride and potassium dichromate, it gives colouring matters of the indamine and saffranine series; and when the base is heated with amidoazobenzene, aniline hydrochloride, and a little aniline, it yields a melt which dissolves in alcohol, forming a dichroic, non-fluorescent solution which appears violet by reflected light, and by transmitted light, red.

Octohydro-α-naphthaquinoline is distinguished by the readiness with which it parts with the hydrogen added on to the "pyridine" nucleus, and undergoes condensation when oxidised. *Ditetrahydro-α-naphthaquinoline*, $C_{26}H_{26}N_2$, is obtained in this way when the octohydro-compound, dissolved in dilute sulphuric acid, is oxidised with potassium dichromate; the intense red colour at first produced disappears slowly, and a voluminous, yellow precipitate of the chromate of the new base separates; this is decomposed by caustic soda, and the base purified by crystallisation from a mixture of chloroform and alcohol. It forms lustrous, white needles, melts at 282°, and is very soluble in benzene and chloroform, much less so in alcohol, and almost insoluble in light petroleum. It does not form an acetyl derivative, is a tertiary base, gives no reaction in chloroform solution with bromine, and does not yield colouring matters with diazotised bases.
W. P. W.

Methanetriquinoïl or Triquinylmethane. By O. Rhoussopoulos (*Ber.*, **24**, 2267—2268).—The author draws attention to the fact that he has already described salts of the compound $CH(C_9NH_6)_3$ (Abstr., 1883, 600), which has been prepared by Noelting and

Schwartz, and named by them triquinylmethane (this vol., p. 1106). The author obtained his salts by the action of quinoline on iodoform and chloroform, and named them methanetriquinoïl hydriodide and methanetriquinoïl hydrochloride, the residue of the quinoline being called quinoïl. E. C. R.

Strychnine. By J. TAFEL (*Annalen*, **264**, 33—84).—Further investigation has shown that the compound named "strychnol" by Loebisch and Schoop (Abstr., 1886, 814), and previously described by the author as strychnine monhydroxide (Abstr., 1890, 1447), is not a phenol, but an imido-acid of the composition

$$C_{20}H_{22}NO(COOH){:}NH,4H_2O\,;$$

so that it may be suitably named *strychnic acid.* The substance, of the composition $C_{21}H_{26}N_2O_4$, obtained by Gal and Etard (*Bull. Soc. Chim.*, **31**, 98) by heating strychnine with a solution of barium hydroxide at 130°, and named by them dihydrostrychnine, loses 1 mol. H_2O at 135°, and has, therefore, the composition $C_{21}H_{24}N_2O_3 + H_2O$; as it is isomeric with strychnic acid, and, also, gives almost all the reactions of the latter, it may be termed *isostrychnic acid.* Both these acids are formed when strychnine is treated with alcoholic soda at 100° or with barium hydroxide at 140°, but the relative quantity of the two compounds depends, to a very considerable extent, on the temperature at which the reaction is carried out; when, for example, finely-divided strychnine (10 parts) is heated at 50—55° with a solution of sodium (1 part) in alcohol (10 parts), strychnic acid alone is formed; but if the temperature is raised to 70°, the product contains small quantities of isostrychnic acid.

Strychnic acid is completely converted into strychnine when it is heated at 190° in a stream of hydrogen; its other properties have been already described by Loebisch and Schoop. The *nitrosamine hydrochloride*, $C_{20}H_{22}NO(COOH){:}N{\cdot}NO,HCl + H_2O$, is obtained when the acid is treated with sodium nitrite and hydrochloric acid in the cold; it crystallises from alcohol in yellowish prisms, is moderately easily soluble in cold water, and gives the nitroso-reaction; on reduction with zinc-dust and acetic acid, it is converted into a compound which reduces Fehling's solution, but when warmed with tin and hydrochloric acid it yields strychnic acid hydrochloride.

Strychnic acid methiodide, $C_{21}H_{24}N_2O_3,MeI + H_2O$, is formed when an aqueous solution of the sodium salt of strychnic acid methiodide (see below) is acidified with dilute acetic acid, and also when methylstrychnine (compare Tafel, *loc. cit.*) is treated with cold hydriodic acid; it loses its water at 120—130°, and is only very sparingly soluble in cold water and alcohol, and insoluble in ether, but it dissolves freely in alkaline carbonates. It gives a nitroso-derivative on treatment with nitrous acid, and, when boiled with dilute acids, it is converted into *strychnine methiodide*, $C_{21}H_{22}N_2O_2,MeI + H_2O$. The *sodium* salt, $C_{22}H_{26}N_2O_3INa + H_2O$, prepared by heating strychnic acid with methyl iodide and alcoholic soda, or by dissolving the methiodide of strychnic acid in methyl alcoholic soda, crystallises in long needles, and is very readily soluble in water and methyl alcohol, but only sparingly in boiling alcohol; the corresponding *silver* salt is a colourless, gelatinous, unstable compound.

Methylstrychnic acid methiodide, $C_{22}H_{26}N_2O_3,MeI + H_2O$, is obtained by treating an aqueous solution of dimethylstrychnine (*loc. cit.*) with hydriodic acid, and, also, together with its methyl salt, by heating a methyl alcoholic solution of the sodium salt of strychnic acid methiodide with methyl iodide. It crystallises from boiling water in small needles, loses its water at 130°, and is moderately easily soluble in hot alcohol, but insoluble in ether; when treated with a little silver nitrate and concentrated nitric acid, it gives the same blood-red coloration as dimethylstrychnine. The *methyl* salt, $C_{22}H_{25}N_2O_3Me,MeI$, separates from boiling water in short needles, and is only sparingly soluble in alcohol and chloroform and insoluble in ether and benzene; when treated with freshly-precipitated silver oxide, it is converted into a strongly alkaline substance which is decomposed on boiling with formation of dimethylstrychnine.

Methylstrychnine (*loc. cit.*) is highly poisonous, and feebly lævorotatory; it gives the same colour reactions as strychnic acid. When treated with nitrous acid in aqueous solution, it is converted into a crystalline nitrosamine, and, when boiled with sodium ethoxide, it is transformed into a feeble base of the composition $C_{24}H_{30}N_2O_3$; this substance crystallises from boiling alcohol in small needles, melts at 158°, and is very readily soluble in benzene, chloroform, and glacial acetic acid, but almost insoluble in water.

A *nitroso*-derivative is obtained as a yellow precipitate when dimethylstrychnine (*loc. cit.*) is treated with amyl nitrite in alcoholic hydrochloric acid solution; it is a semi-crystalline, very deliquescent powder, and when dried at 100° in an atmosphere of hydrogen, it has the composition $C_{23}H_{29}N_3O_4Cl_2$.

Isostrychnic acid, $C_{20}H_{22}NO(COOH){:}NH + H_2O$, is best prepared by heating strychnine (100 grams) with crystalline barium hydroxide (150 grams) and water (800 grams) at 135—140°, then filtering from unchanged strychnine, and saturating the hot filtrate with carbonic anhydride; the acid is extracted from the precipitated barium carbonate with dilute soda. The anhydrous compound is very hygroscopic, and takes up 1 mol. H_2O on exposure to the air; it resembles strychnic acid very closely, than which, however, it is rather more sparingly soluble in water. It gives the same colour reactions as strychnic acid, even after it has been boiled with acids, and it is not changed by boiling concentrated hydrochloric acid; it forms an oily acetyl derivative and an oily ethyl salt, and is highly poisonous. The *hydriodide*, $C_{21}H_{24}N_2O_3,HI + 2H_2O$, crystallises in well-defined prisms and loses 1 mol. H_2O over sulphuric acid in a vacuum, the other being expelled at 110°; it is readily soluble in hot water, but only sparingly in cold water and alcohol, and insoluble in ether. The *nitrosamine hydrochloride*, $C_{21}H_{23}N_3O_4,HCl + 2H_2O$, crystallises from hot alcohol in needles, and is readily soluble in warm water, but insoluble in ether; it is decomposed by boiling water, gives Liebermann's reaction, and, when warmed with tin and hydrochloric acid, is decomposed, with formation of strychnine.

Isostrychnic acid methiodide, $C_{21}H_{24}N_2O_3,MeI$, can be prepared by treating the sodium salt (see below) with dilute mineral acids, or by the action of hydriodic acid on an aqueous solution of isomethylstrychnine; it separates from hot water in crystals, is only sparingly soluble in alcohol, and insoluble in ether; when treated with nitrous acid, it yields a resinous nitroso-derivative. The *sodium* salt, $C_{22}H_{26}N_2O_3INa + H_2O$, obtained by warming isostrychnic acid with methyl iodide and sodium methoxide in methyl alcoholic solution, crystallises from hot alcohol in microscopic needles, and is readily soluble in water.

Methylisostrychnic acid methiodide, $C_{22}H_{26}N_2O_3.MeI + H_2O$, is obtained, together with its methyl salt, by heating the sodium salt of isostrychnic acid methiodide with methyl iodide in methyl alcoholic solution, or by treating isodimethylstrychnine with hydriodic acid; it crystallises from boiling water in needles, loses its water at 130°, melts at 270—275° with decomposition, and is moderately easily soluble in hot alcohol, but insoluble in ether, chloroform, and benzene. The *methyl* salt, $C_{22}H_{25}N_2O_3Me,MeI + 2H_2O$, crystallises from boiling water in long needles, loses its water in a vacuum, and is very sparingly soluble in alcohol, and insoluble in ether and benzene; when treated with freshly-precipitated silver chloride, it is converted into the corresponding *methochloride*, $C_{22}H_{25}N_2O_3Me,MeCl + 2H_2O$, which crystallises in long, colourless needles.

Isomethylstrychnine, $C_{22}H_{26}N_2O_3 + 7H_2O$, is formed when an aqueous solution of isostrychnic acid methiodide is treated with silver oxide, first at the ordinary temperature and then at 100°; it crystallises from hot water in small, colourless needles, and is very readily soluble in alcohol and hot water, but insoluble in ether and benzene; it yields a crystalline nitrosamine, and it gives the same reaction with dilute sulphuric acid and potassium dichromate as methylstrychnine, even after having been boiled with dilute acids.

Isodimethylstrychnine, $C_{23}H_{28}N_2O_3 + 3H_2O$, prepared from methylisostrychnic acid methiodide in like manner, or from the methylhydroxide of methyl methylisostrychnate, as previously described in the case of dimethylstrychnine (*loc. cit.*), separates from hot water in well-defined crystals, and is readily soluble in alcohol, but insoluble in ether; it gives the same reactions with oxidising agents and with nitrous acid as dimethylstrychnine.

The author's experiments have shown that the so-called hydrates of strychnine are isomeric imido-acids, that strychnine is an inner anhydride of strychnic acid, and that methyl and dimethylstrychnine are betaïn-like derivatives of this acid; the nitrogen atom in the $-CO-N\equiv$ group in strychnine is in direct combination with one benzene nucleus. F. S. K.

Constitution of Pseudephedrine. By W. Filehne (*Virchow's Archiv*, **124**, 95—96).—Of the three possible constitutional formulæ advanced by Ladenburg (Abstr., 1889, 1020) for this mydriatic alkaloïd, the one he regards as most probable is

$$OH{\cdot}CHPh{\cdot}CHMe{\cdot}NHMe.$$

In this formula the amido-group stands in the β-position, and the substance would then be analogous to β-tetrahydronaphthylamine

and phenylethylamine. The complete analogy now found for these substances, as regards their physiological action, confirms this supposition.
W. D. H.

Benzoylpseudotropeïne, an Alkaloïd of Java Coca-leaves. By C. LIEBERMANN (*Ber.*, **24**, 2336—2345).—The alkaloïd was obtained in the form of its hydrobromide from Dr. Giesel, and was purified by extraction with ether and crystallisation from boiling water.

Benzoylpseudotropeïne hydrobromide, $C_8H_{14}NOBz,HBr$, crystallises in beautiful, long leaflets, and is soluble in water and alcohol.

Benzoylpseudotropeïne, $C_8H_{14}NOBz$, is obtained by decomposing the above salt with sodium carbonate and extracting with ether. On evaporating off the ether, it is obtained as an oil which solidifies in radiating crystals. It melts at 49°, reacts strongly alkaline in alcoholic solution, is easily soluble in alcohol, ether, chloroform, benzene, and light petroleum, and is optically inactive. The *hydrochloride*, obtained by passing hydrogen chloride into an ethereal solution of the base, crystallises in white needles, and melts at 271°. The *platinochloride* is obtained as a flesh-coloured precipitate, and is insoluble in water, alcohol, and ether. The *aurochloride* crystallises from water in beautiful, yellow needles, melts at 208°, and is sparingly soluble. Mercuric chloride causes a crystalline precipitate when added to a solution of the hydrochloride. Picric acids give a sparingly soluble precipitate, crystallising in yellow needles.

When the above base or its salts is heated with hydrochloric acid in a reflux apparatus for some hours, it is completely decomposed into benzoic acid and pseudotropine.

Pseudotropine, $C_8H_{15}NO$, is obtained from the products of hydrolysis of the above base after the benzoic acid has been extracted with ether. The acid solution is evaporated to dryness, and the hydrochloride either decomposed with silver oxide or excess of strong sodium hydroxide is added, and the base extracted with ether. It has a strongly alkaline reaction, crystallises in beautiful needles, melts at 106—107°, boils at 240—241° (corr.), and is easily soluble in water, alcohol, and benzene, and is precipitated from the latter solvent by light petroleum. The base is, no doubt, identical with Ladenburg's pseudotropine, although the aurochloride melts at 225°, whereas Ladenburg's melted at 198°. The *hydrochloride* crystallises in needles, is somewhat hygroscopic, and easily soluble in alcohol. The *aurochloride* crystallises from water in beautiful, yellow needles, and is easily soluble in alcohol and hot water. The *platinochloride*, when first prepared, is so soluble that it is necessary to evaporate the solution almost to dryness before crystallisation takes place; the crystallised salt is, however, difficult to dissolve in water, and is precipitated on the addition of alcohol. Pseudotropine hydrochloride yields, with mercuric chloride, a white precipitate; with picric acid, an easily soluble salt, crystallising in yellow needles.

The author has synthesised benzoylpseudotropeïne by heating pseudotropine (3 grams) with water (1·5 grams) and benzoic anhydride ($1\frac{1}{4}$ mols.) on the sand-bath for $1\frac{1}{4}$ hours at the boiling point of the mixture. The synthetical base is entirely similar to the natural one.

The author has no doubt that a series of pseudotropeïnes, corresponding to the tropeïnes, can be prepared from pseudotropine. He has prepared the following:—

Cinnamylpseudotropeïne, $C_8H_{14}NO(C_9H_7O)$, is obtained from pseudotropine and cinnamic anhydride, melts at 87—88°, and is very easily soluble in cold alcohol, ether, and benzene, somewhat less so in light petroleum. The *hydrochloride* is obtained as a white, crystalline precipitate on passing hydrogen chloride into an ethereal solution of the base, and is easily soluble in alcohol and ether. The picrate, platinochloride, and aurochloride are similar to those of benzoylpseudotropeïne. E. C. R.

Alkaloïds of Corydalis cava. By F. ADERMANN (*Chem. Centr.*, 1891, i, 978—979).—The dried and ground-up roots of *Corydalis cava* are extracted with 80—85 per cent. alcohol at 25°, the alcohol evaporated under diminished pressure, and the residue extracted by Dragendorff's method. Benzene extracts considerable quantities of crystalline substances, both from the acid, and also from the alkaline liquid. The alkaline liquid may be extracted firstly with light petroleum, and then with chloroform, the latter extracting an alkaloïd. Ether extracts alkaloïds from the acid liquid, and if, after separating the ether, the solution be extracted with chloroform, a base is obtained which is identical with that obtained from the alkaline liquid with the same reagent. The author isolated three bases. The first is isomeric with the hydroberberine of Court, $C_{20}H_{21}NO_4$, and is oxidised by chromic acid to berberine. It differs from Court's hydroberberine in the melting point, 138°, and in its optical properties; it is a tertiary monamine.

The chloroform extract of the *Corydalis* alkaloïds includes one which is similar to caffeïne; its formula is $C_{22}H_{21}NO_4$. It reacts with concentrated sulphuric acid, forming a yellowish coloration, which passes, slowly in the cold, rapidly when warmed, into a beautiful violet. Erdmann's reagent causes a brownish-red coloration, Fröhde's, a violet, or green streaked with reddish-violet; selenium sulphuric acid, a light violet; nitro-sulphuric acid, a bluish-violet; and potassium dichromate and sulphuric acid, a similar coloration to strychnine. If the solution of the base be covered with concentrated hydrochloric acid and chlorine water added, a red zone is formed, and, after shaking the mixture the whole solution becomes pink-coloured. The author names this base *corydaline*. It resembles Reichwald's fumarine, $C_{21}H_{19}NO_4$ (Abstr., 1890, 272), in some respects, but differs from it in being optically active and in its solubility. The third base which the author extracted was not obtained crystalline, but reacted with the several alkaloïd reagents. J. W. L.

New Alkaloïd in Tylophora asthmatica. By D. HOOPER (*Pharm. J. Trans.*, **21**, 6—7).—The inspissated alcoholic extract of the root of *Tylophora asthmatica* treated with water gives a solution which, after filtration, is made alkaline with ammonia, and agitated with ether to extract the alkaloïd *tylophorine*. This, on evaporating its ethereal solution, is left in the form of crystals, sparingly soluble in water. The ethereal and alcoholic solutions have an alkaline reaction, and the substance forms with acids neutral solutions, from which it is precipitated by all the usual alkaloïdal reagents. The *nitrate* and *hydrochloride* form prismatic crystals. When added to sulphuric acid, the pure alkaloïd is dissolved with colorations successively reddish-brown, red, green, and finally blue. Nitric acid colours it purple-red, dissolving some to orange solution; hydrochloric acid forms a yellow solution, Fröhde's reagent dissolves it with a sap-green coloration; and sulphuric acid and potassium dichromate produces a violet-brown liquid. It decolorises potassium permanganate, but is not affected by ferric chloride or lead acetate. R. R.

Influence of Oxygen on the Formation of Ptomaïnes. By W. HUNTER (*Proc. Roy. Soc.*, **49**, 376—379).—The interest attaching to the *rôle* of oxygen in the life history of bacteria led to this investigation of the quantity of ptomaïnes formed by means of putrefaction bacteria, (1) when oxygen was freely admitted; (2) when it was present in limited quantity; and (3) when it was withheld altogether. Such ptomaïnes as the diamines, formed in the early stages of putrefaction, are not poisonous, and contain no oxygen; in this respect they differ from those containing oxygen, like muscarine and neurine. Brieger concluded from this that free access of oxygen plays an important part in the formation of the poisonous bases, and favours the formation of ptomaïnes generally. The chief result of the present research is that the formation of ordinary putrefaction ptomaïnes is favoured by an entire absence of oxygen.

The ptomaïnes were isolated by Brieger's method, and in connection with the diamines accurate quantitative results were obtained by the use of benzoic chloride (the method of Baumann and Udránszky). The diamines formed during the early stages of the process (without oxygen, none being obtained if oxygen was admitted freely) disappear as putrefaction proceeds. No very definite results regarding toxic alkaloïds were obtained; symptoms of poisoning were only obtained in one instance (eight experiments in all being made) from the injection of a fluid which had putrefied in the absence of oxygen.

W. D. H.

Peptotoxin. By E. SALKOWSKI (*Virchow's Archiv*, **124**, 409—454). As a result of experiments on the digestion of proteïds by means of pepsin, no poisonous substance soluble in water and amyl alcohol was formed, such as Brieger states he isolated from digested fibrin; in other words, a "peptotoxin" in Brieger's sense of alkaloïdal substance does not exist.

If putrefaction is prevented, leucine and tyrosine are also never formed in gastric digestion.

If putrefaction be allowed to occur, poisonous basic products make their appearance. Some specimens of meat contain poisonous bases previous to the occurrence of digestion at all. The resinous substance present in commercial amyl alcohol (compare Udránszky, Abstr., 1887, 1133) is also toxic. These facts no doubt explain Brieger's error.

That albumoses and peptones are toxic none will deny; the object of the present research is to show that their toxicity is one of their inherent properties, and not due to any basic product or toxine separable from them. W. D. H.

Harnack's Ash-free Albumin. By B. Werigo (*Pflüger's Archiv*, **48**, 127—149; compare Abstr., 1890, 272 and 392). The so-called ash-free albumin obtained by Aronstein and Schmidt by means of dialysis was shown by later observers (Heynsius, Winogradoff) to be poor in ash, but not free from ash, and, moreover, that its characteristic properties (uncoagulability by heat, solubility in water, &c.) were due to the use of alkali in its preparation. Harnack has lately taken up the question again, and prepared a proteïd substance practically free from ash, by precipitating it by means of hydrochloric acid from a solution of copper albuminate in sodium hydroxide. This material agrees in its properties with the substance obtained by Aronstein. The present researches first show that in his main facts Harnack is quite correct, the only point of difference being that in order to precipitate the ash-free proteïd, it is necessary to add excess of hydrochloric acid; mere neutralisation precipitates only the copper albuminate. Further investigation of the ash-free proteïd showed that it is not coagulable by heat, but that it is precipitated by neutralisation, the precipitate being soluble in excess of either acid or alkali; in other words, the substance which Harnack describes as ash-free albumin is only a derivative of albumin, which resembles in its properties the well-known derivatives called acid-albumin and alkali-albumin.

In Harnack's case one deals with an acid solution, in Aronstein's with an alkaline solution, of this albuminate; this accounts for a difference which must be noted in the two cases. The reaction sufficiently explains this fact, which is that Harnack's substance is, and Aronstein's is not, precipitable by neutral salts. Aronstein's substance, however, like all these albuminates, is coagulated by heat when their solutions are saturated with such neutral salts.

The next question which arises is whether Harnack's derived albumin is formed by the alkali and acid used in the latter parts of the process of preparation, or previous to this. A number of considerations, none, however, absolutely proving the point, appear to show that the change occurs prior to the use of the alkali and acid; or, in other words, that Harnack's copper albuminate is strictly analogous to the albuminates known as acid- and alkali-albumin respectively; in the one case copper, in the other case acid and alkali are in union with the proteïd molecule. It has already been stated that in the preparation of Harnack's albuminate it is necessary to add excess of acid; whereas after its preparation it is readily soluble in slight excess of acid. This difference is due to the fact that during the addition of hydrochloric acid to the sodium hydroxide solution sodium chloride is formed; and it is the presence of this salt which renders the albuminate insoluble in the excess of acid; this is true for acid-albumin generally.

Weighed quantities of Harnack's albuminate were then subjected to titration, the quantity of standard acid and alkali necessary to precipitate and redissolve the precipitate being noted. From these the amount of sodium present in the alkali-albuminate was calculated, the average of six experiments showing a percentage of 0·969. Two atoms of sodium in the molecule, taking Harnack's estimation of the molecular weight of albumin (4740·8) as correct, would amount to 0·97 per cent. Harnack's copper albuminate, however, is stated to contain 2 atoms of copper; the sodium compound, if analogous, should therefore contain 4 atoms of sodium.

Further experiments showed that in some cases for precipitation and re-solution two equivalents of alkali correspond to one of acid, and a number of arguments are advanced for and against the contention that Harnack's formula should be doubled; the facts are, however, not irreconcilable with the assumption that Harnack's formula is correct; and there appears to be no doubt that acid and alkaline albuminates are definite chemical compounds. W. D. H.

Behaviour of Albumin when Subjected to Pressure. By A. Denaeyer (*Chem. Centr.*, 1891, i, 509; from *Compt. rend. Stat. Sci. Brasserie de Gand.*, 1 Heft).—Albumin, when heated under pressure either in water or in dilute acids, undergoes changes. When heated in water under a pressure of one atmosphere, it becomes soluble again and reacts as uncoagulated albumin. At higher pressures other changes take place, the solution becomes more perfect, and leucine and tyrosine are formed. At very high pressures, for instance, 10 atmospheres, the solution becomes alkaline, and ammonia derivatives and amido-acids are formed. A small quantity of albumose, precipitable by ammonium sulphate, has been detected as a result of the action, but no peptone. The albumin of egg, muscle, blood, and milk caseïn all behave similarly under these conditions.

Treatment with dilute hydrochloric acid causes a simple solution of albumin; by boiling it with 10 per cent. hydrochloric acid, a solution is obtained from which nitric acid causes no precipitation, nor is the albumin precipitated after neutralising the acid with soda or potash. By heating the albumin with 5 per cent. hydrochloric acid under a pressure of one atmosphere for one hour, a similar solution is obtained. This modification the author names *α-acid albumin.* If the heating be continued for two hours, or if the pressure be increased to 2 atmospheres, a clearer solution is obtained which is neither precipitated by boiling nor by nitric acid, but is precipitated by neutralising the acid; this modification has been named *β-acid albumin.* No peptone could be detected. They are similar to syntonin. At higher pressures considerable quantities of ammonium chloride and chlorine derivatives of the amido-acids are formed. J. W. L.

Physiological Chemistry.

Human Respiration, Air being Re-breathed in a Closed Vessel. By W. MARCET (*Proc. Roy. Soc.*, **49**, 103—117).—The following are the results obtained in the present enquiry:—

1. On re-breathing air in a closed vessel, less carbonic anhydride is expired within a given time than in ordinary breathing, the volume of the air undergoing at the same time a slight reduction.

2. When fresh air is taken after re-breathing air in a closed vessel, the volumes of air breathed and the weights of carbonic anhydride expired are greater than in ordinary breathing; this, however, passes off in a few minutes. W. D. H.

The Respiratory Exchange of Gases. By W. MARCET (*Proc. Physiol. Soc.*, 1891, 33—35).—A number of data concerning the amount of gases inspired and expired by human individuals are given. They were obtained by the use of the author's own apparatus. The mean respiratory quotient in 22 experiments was 0.87. The influence of food and fasting on the amount of gases respired is also illustrated. In five experiments, each lasting five minutes, the air inspired contained 3 to 4 per cent. of carbonic anhydride. Under these circumstances, the amount of oxygen consumed is greater, while the carbonic anhydride expired is very much less, than in ordinary breathing. W. D. H.

Action of Paraffinic Nitrites on Blood Pressure. By J. T. CASH and W. R. DUNSTAN (*Proc. Roy. Soc.*, **49**, 314—319).—Amyl nitrite is the one on which most of our knowledge at present rests. This and other nitrites of the paraffinic series were prepared pure for the present research by the reaction of the corresponding alcohol, previously purified, with sodium nitrite in the presence of dilute acid. The blood pressure was recorded by means of a modification of the ordinary kymograph, by which it was possible to record a long tracing on a slowly revolving drum, and shorter tracings at intervals on a rapidly revolving cylinder. By means of experiments on cats and rabbits, it was shown that the well-known effect of a fall in blood pressure produced by amyl nitrite is due to the direct action of the drug on the vascular walls causing the vessels to dilate (Brunton, Mayer, and Friedrich), and not to its action on the vaso-motor centre (Filehne). These experiments fall into two categories; in the first, the head was cut off from the circulation, and amyl nitrite still gave rise to as great a fall of pressure as when the head was included in the circulation. In the second series, the drug was injected into the carotid artery, but prevented from reaching the general circulation by appropriate ligatures. The fall of pressure did not occur until these ligatures or clamps were removed.

In experiments on man, a special nose and mouth piece was devised to enable a known quantity of the nitrite to be inhaled. The order of activity (that is, extent of pulse acceleration, which is greatest in neurotic individuals) for various nitrites is :—(1) α-amyl; (2) β-amyl; (3) isobutyl; (4) secondary butyl; (5) primary butyl; (6) secondary propyl; (7) primary propyl; (8) ethyl; (9) methyl.

A broad summary of the action of the nitrites is as follows :—

All produce a fall of blood pressure, and an accompanying acceleration of the pulse; the latter is not so marked after intravascular injection as after inhalation, and is also less marked in cats than in men. The respiration is affected temporarily during inhalation in various degrees by the different nitrites, and permanently by repeated administration of the same or different nitrites.

The activity of the nitrites, as measured by the fall in blood pressure after inhalation, is as follows :—(1) secondary propyl; (2) tertiary butyl; (3) secondary butyl; (4) isobutyl, nearly equal; (5) tertiary amyl; (6) α-amyl; (7) β-amyl, nearly equal; (8) methyl; (9) butyl; (10) ethyl; (11) propyl. After intravascular injection, however, the order is nearly the reverse. The causes of these differences will be considered in a later paper. W. D. H.

Influence of Temperature on Digestive Ferments. By E. Biernacki (*Zeit. Biol.*, **28**, 49—71).—Digestive ferments require for their efficient action a certain reaction and a suitable temperature. The *optimum* temperature is 39—40°, that is, a little over that of the body. Higher temperatures destroy the ferment, and the present research is occupied with the determination of the temperature necessary for this latter purpose.

The first ferment investigated was trypsin, and it was found that 45° C. markedly lessens its activity, and exposure for five minutes to 50° destroys it altogether. The specimens of trypsin employed were some pure, some impure, and certain exceptions to the above stated rule were noted. It being very improbable that various trypsins differ in this particular, in virtue of their inherent characters, experiments were instituted to determine the factor that caused the difference. It was found that small admixtures with certain salts had the power of increasing the resistance of the ferment to temperature; the activity of the ferment was often lessened by the salt (although this was more marked in the case of pepsin), but the *optimum* temperature was 50°; 55° lessened, and 60° destroyed, the activity of the ferment. The salts which acted thus were ammonium sulphate (a salt used in the preparation of some specimens of ferment used in the preliminary experiments), ammonium chloride, phosphate, and nitrate, and sodium chloride. If mixtures of two or more of these salts were used, the effect was more marked still.

Certain salts (ammonium carbonate and oxalate, magnesium sulphate, sodium sulphate and phosphate), starch, and sugar had no such action, but certain products of proteolytic activity (albumose, amphopeptone, and antipeptone) act like the salts just enumerated. All the materials that act in this way increase the alkalinity of the digesting medium; minute doses of sodium hydroxide act in a precisely similar way, and the proposition is advanced that the whole of the phenomena are simply dependent on the reaction. Increase of alkalinity protects the ferment. It was found that increase of acidity (trypsin will act in an acid medium if salicylic acid be employed) acts in exactly the opposite way; in an acid medium, 33—35° is the *optimum* temperature; 40° hinders, and 45° destroys, the action of the ferment.

Pepsin was then investigated, and it was found that acidity acts towards this ferment precisely like alkalinity towards the tryptic ferment, the temperature necessary to destroy its activity rising from 65° to 70°. In a neutral medium, the temperature falls to 55°.

Unfiltered fresh saliva loses its diastatic properties at 75°, filtered saliva at 70°, diluted saliva at 60°, pure ptyalin at 70°, unless its solution is much diluted, when the necessary temperature sinks to 60°. The influence of salts, reaction, &c., is exactly the same in kind as with trypsin. In all cases, if the pure ferment be used, the influence of temperature and the influence of salts, &c., on the temperature are more easily observed than if the ferment be impure, as contained, for instance, in the digestive juice.

The explanation of these occurrences probably lies in the formation of loose compounds with the enzymes, analogous to the pepsin-hydrochloric acid of Schmidt and other authors. W. D. H.

Action of Pancreatic and Rennet Extracts on Caseïn. By J. S. Edkins (*Brit. Med. J.*, i, 1891, 1332—1333, and *J. Physiol.*, **12**, 193—219).—Milk is occasionally clotted by pancreatic extracts; but even if this does not occur, the caseïn in the milk (that is, caseïnogen, W. D. H.) will be altered so that boiling causes a curdling of the milk. The caseïn thus altered has been termed meta-caseïn (Roberts). The existence of meta-caseïn is, however, transient. Its appearance is not due to the combined action of heat and fatty acid liberated by the pancreatic juice, as no change in reaction occurs if the juice used has lost its piolytic properties, and yet meta-caseïn appears. Meta-caseïn appears to be caseïn of which the precipitation is hindered in the cold by the concomitant action of trypsin. Meta-caseïn may be separated from milk by half saturation with certain neutral salts. Its reactions suggest affinities to caseïn rather than caseïnogen. Whey proteïd appears to come into existence simultaneously with the appearance of meta-caseïn. W. D. H.

Influence of Alcohol on Proteïd Metabolism. By R. H. Chittenden, C. Norris, and E. E. Smith (*J. Physiol.*, **12**, 220—232).—As the result of three experiments on dogs, the conclusion is drawn that alcohol has no striking action on the general metabolism of proteïd matter. In each case they extended for eight or ten days, and the quantity of alcohol used was large, rising to 2·5 c.c. per kilo. of body weight. At the same time alcohol has some specific action on nutrition, as manifested in its tendency to increase the excretion of uric acid in proportion to urea. W. D. H.

The Proteïd Requirement of Healthy Men. By Studemund (*Pflüger's Archiv*, **48**, 578—591).—Voit gives the following daily diet as a minimal one for a full-grown man: 118 grams proteïd, 56 grams fat, and 500 grams carbohydrate. Since his time various observers have given other numbers; most interest attaches to the daily proteïd requirement, and various authors give numbers from 110 to 35 grams. These variations are in part due to the fact that the number of individuals on whom the observations were made was small, being often limited to the experimenter's own person. It is impossible to deduce an average diet from such observations, but it is necessary to experiment on large numbers of persons. Accordingly, in the present research, continuous observations on 47 recruits in the army were made. These lasted for nearly four months. The experiments involved daily examination of the food and body weight; the food included the ordinary rations, the purchases of the recruits, and the packages of eatables they received from their homes. In this way, all were not on precisely the same diet, but the results are all averaged up, and the daily mean diet was thus, 113 grams proteïd, 54·3 fat, and 551·8 carbohydrate. At the end of the period, 34 of the men had gained in weight, five had lost weight, and three were the same as at the beginning; one died, and the remaining four did not continue the experiment. On the average each man gained 3·5 kilos. in weight, or 38 grams per day. This increase of weight was doubtless due chiefly to growth of muscle (the daily exercises of these men are given); and thus 7·6 grams or 20 per cent. of the increased weight may be taken as the amount of new proteïd put on daily; this would reduce the daily requirement of proteïd food to 105·4 grams, which is a smaller number than that given by Voit as the amount necessary to keep the body in equilibrium. W. D. H.

Nutrition of Muscle. By J. BRINCK (*Brit. Med. J.*, ii, 1891, 181—183).—The object of these experiments was to test on skeletal muscle the nutritive action of various proteïd fluids in continuation of the results which Kronecker and his pupils have obtained on cardiac muscle (Abstr., 1889, 632). These results are to the effect that solutions of myosin, syntonin, peptone, caseïn, egg albumin, and glycogen are incapable of restoring to activity the "washed out" frog's heart, and that serum albumin is the only known nutritive proteïd. Ringer attributes the resuscitating effect of a circulating fluid to its inorganic salts, and Mays (*Practitioner*, **39**, No. 4) to creatine and its allies.

A "washed out" heart is one perfused by normal saline, until it ceases to respond to strong induction shocks, not when it ceases to contract spontaneously. Ringer apparently uses the word in the latter sense, and his results are explained by regarding his solutions as stimulant, not nutritive. The present experiments made with the sartorii of the frog lend support to Kronecker's conclusion that the proteïds of serum (spoken of in the authoress's paper roughly as serum albumin) are nutritive, and that other proteïds, salts, and extractives are not. W. D. H.

Effect of Partial Extirpation of the Kidneys on Nutrition. By J. R. BRADFORD (*Proc. Physiol. Soc.*, 1891, 18—20).—Dogs were fed on a known diet, and the daily amount of urine and urea determined. The total nitrogen of ingesta and excreta was determined by Kjeldahl's method.

A wedge-shaped portion of one kidney was removed antiseptically, and after the healing of the wound, the animal is apparently normal. The kidney wound heals by the first intention. From a fortnight to six weeks after this first operation, the whole of the second kidney was removed. The animal rapidly emaciates; its temperature falls, and death ensues from two to six weeks after the second operation. The urine contains no albumin or sugar, but the most remarkable effect observed is that the animal which only retains a fragment of one kidney secretes a markedly increased amount of urine, of urea, and of total nitrogen. If, however, the fragment removed at the first operation is small, so that less than about three-quarters of the whole kidney weight is removed at both operations, there is no increase in urea, but merely in the water excreted; the animal emaciates but slightly and lives much longer.

The fragment of kidney found *post mortem* is distinctly atrophied.

Corresponding with the increase of urea in the urine, there is an increase also in the blood (here it may be quadrupled), muscles, liver, and brain. Control experiments with normal dogs were made.

W. D. H.

The Influence of Sodium Chloride in the Chemical Composition of the Brain. By I. Novi (*Pflüger's Archiv*, **48**, 320—335).—The injection of a 10 per cent. solution of sodium chloride into the carotid artery leads to a loss of water in the brain, which is especially marked in the cortex. Less than 1·25 per cent. of the total amount of water in the brain is thus lost after one injection, but after injections repeated at intervals, the loss may amount to 5 per cent. The normal amount of sodium in the brain rises, that of potassium falls; the sum of the two metals is, however, almost constant. This is especially the case if one considers the brain as a whole; in the grey matter, the greater metabolic activity leads to variations within somewhat wider limits. In the whole brain, the sodium rises from 0·09 to 0·32, and the potassium falls from 0 39 to 0·25 per cent. The percentage of chlorine also rises, for sodium requires more chlorine to saturate it than the same weight of potassium. To these changes the convulsions that occur are probably due. It was also noted that other effects were a clear red colour of the venous blood, and an excitability of muscular and nervous tissues, lasting many hours after death.

W. D. H.

Deposits of Iron and Glycogen in the Tissues. By S. Delépine (*Proc. Physiol. Soc.*, 1891, 35—39).—The most convenient microchemical test for so-called "free iron" in the tissues is the Prussian blue reaction. The specimens are first placed in a 5 to 10 per cent. solution of potassium ferrocyanide, washed in water, and lastly, for a period varying from a few minutes to a few hours, in a 0·5 to 1 per cent. solution of hydrochloric acid.

Hæmoglobin does not give the test; and the term "free iron" is apparently used for loose combinations of iron with nucleïn or other albuminous material deposited in the cells, and generally colourless, although in the kidney it occurs in the form of brownish granules. The kidney gives the test more readily than the liver; the organs used were from a case of doubtful pernicious anæmia. The liver, however, gives the reaction well after a few days immersion in alcohol and glycerol, which are considered to produce a loosening of the union between the iron and the organic compound. The conclusion is drawn from this that the iron is more firmly combined in the liver than in the kidney cells.

A new method recommended for the making of permanent specimens to show deposits of glycogen or lardaceïn in cells is the following:—The sections are washed with a solution of iodine in chloroform, dehydrated with alcohol, cleared with clove oil, and mounted in chloroform balsam coloured with iodine. W. D. H.

Lecithin in the Liver. By A. HEFFTER (*Chem. Centr.*, 1891, i, 459; from *Inaug. Diss. Leipzig*, 1890).—The author finds that the amount of lecithin present bears a definite relation to the weight of the liver, that an alteration of food does not affect this, but that the proportion decreases during a long fast. Phosphorus poisoning is accompanied by a material decrease, upwards of 50 per cent., in the quantity of lecithin in the liver, and the decrease is the greater the more fatty the liver. The author considers that this is occasioned by the direct decomposition of the stored-up lecithin. J. W. L.

Composition of the Bones of Aged Rabbits. By L. GRAFFENBERGER (*Landw. Versuchs-Stat.*, **39**, 115—126).—Hitherto the composition of the bones of rabbits of 6—8 years old has not been made known. The author now communicates the complete composition of the bones of a buck 6½ years old and a doe 7½ years old.

The results as stated, accompanied by full analytical details, are: water and fat decrease with increasing age; there is no change between the ratios of organic to inorganic matter; old rabbits' bones contain more carbonate but less phosphate of lime than the bones of the young animals, 2—4 years. E. W. P.

Amount of Fat and Dry Matter in the Milk of some Hill-bred Cows. By J. SIEDEL (*Bied. Centr.*, **20**, 393—394; from *Wien. landw. Zeit.*, **41**, 166).—Milk of cows of the Pinzgau, Mürzthal, and Murboden breeds was examined. The cows were kept for several weeks on the same food. The daily feeding was:—Malt (1·8 kilos.), wheat bran (1·8 kilos.), clover hay (3·5 kilos.), meadow hay (10 kilos.), and salt (25 grams). The cows were fed three times daily, and the specially good ones were milked three times daily. The average composition of the milk from the different breeds was as follows:—

Breed.	Daily yield.	Sp. gr.	Fat per cent.	Dry matter per cent.
Murboden	8·9 litres	1·0330	4·05	13·24
Mürzthal	10·4 ,,	1·0318	3·58	12·48
Pinzgau	7·4 ,,	1·0338	3·78	12·08

Owing to the cows of the first two breeds having been specially selected as good milking cows, and to the different ages of the cows, no direct comparison with regard to the yield of milk can be made. The average weight of the Murboden and Mürzthal cows was 580 kilos., whilst the weight of the Pinzgau cows varied from 400 to 500 kilos. N. H. M.

Citric Acid a Normal Constituent of Milk. By T. HENKEL (*Landw. Versuchs-Stat.*, **39**, 143—151).—To obtain citric acid from milk, freshly separated milk was curdled with a strong solution of rennet, the caseïn separated, and then 10 c.c. normal acetic acid and 10 grams "Spanish-earth" per litre were added, and the mixture boiled, filtered, and neutralised with milk of lime. On concentrating the filtrate, a powdery precipitate is formed, which, when washed first with water, and then with ether alcohol, gave all the reactions for calcium citrate. More especially was the reaction with Sabanin-Laskowski's reagent marked, this reagent being only active with citric and aconitic acids. Experiments showed that citric acid existed in the milk, and is not produced or introduced by the rennet, so that it must be considered as a normal constituent. E. W. P.

Origin of Citric Acid in Milk. By A. SCHEIBE (*Landw. Versuchs-Stat.*, **39**, 153—170).—The source of citric acid in milk, as well as the various methods whereby it may be estimated, as also the experiments made which have given rise to the first method employed, are here detailed.

The source is still uncertain, for the acid is to be found in cows', goats', and woman's milk when food such as bread, peas, &c., has been supplied which contains no acid. Henkel (see previous paper) failed to find citric acid in human milk, but this was probably due to the fact that 1 milligram per litre of lactose prevents the Sabanin-Laskowski reaction from working.

As regards the method recommended for quantitative estimation, 400 c.c. of milk is mixed with 4 c.c. N. $2\frac{1}{2}$ sulphuric acid, boiled, and then 10 grams of "Spanish-earth," previously made into a paste with water, is added, boiled, and when cool made up to $\frac{1}{2}$ litre. To 100 c.c. of filtrate (= 80 c.c. milk), baryta-water is now added to bring back the milk to its usual acidity, and then evaporated to a syrup, but just before this syrup is quite cool 3·2 c.c. N. $2\frac{1}{2}$ sulphuric acid is added, to set the citric acid free 20 c.c. of absolute alcohol is gradually added, and later on 60 c.c. of ether, the liquid filtered, and the residue (lactose) washed with ether alcohol. To the filtrate, alcoholic ammonia is added until a permanent opalescence is produced, and the ether distilled off until only 20 c.c. of residue is left, to which 60 c.c. of absolute alcohol is added. It is now heated to boiling on a water-bath, and then 10 c.c. of alcoholic ammonia added, whereby the citric acid is completely precipitated. This precipitate contains, besides ammonium citrate, ammonium sulphate and phosphate and a small amount of chloride, and a trace of organic matter, all of which may be removed by a second precipitation; add 1 c.c. N. $2\frac{1}{2}$ sulphuric acid and 1 c.c. water, then add 60 c.c. of absolute alcohol, and precipitate with 10 c.c. of alcoholic ammonia; as it requires a long time for the liquid to clear, it is advisable to add ammonium carbonate and heat in a retort with a reflux condenser, then filter, and wash with absolute alcohol; now dissolve the citrate in 20 c.c. water, add excess of a titrated solution (20—30 c.c.) of potassium dichromate (46·1 grams per litre) and 20—25 c.c. of concentrated sulphuric acid; heat (not boil) for $\frac{1}{4}$ hour. Dilute the brownish-green solution with 50 c.c. of water, add excess of titrated solution of ferrous ammonium sulphate until a clear green is produced, and then titrate back, the final reaction being noted by potassium ferricyanide. 4·61 grams of dichromate are equivalent to 1 gram of citric acid.

To detect citric acid qualitatively, the precipitate formed after heating with ammonium carbonate is dissolved in water, evaporated to 1 c.c., 3 c.c. of a concentrated solution of ammonia added, and then finally the Sabanin-Laskowski reagent.

In human milk, 0·54 gram citric acid per litre has been found; this is about half of that in cows' milk, whilst in goats' milk 1—1·5 gram per litre has been estimated. E. W. P.

Nitrogenous Substances in Human Urine. By W. CAMERER (*Zeit. Biol.*, **28**, 72—104; compare Abstr., 1890, 1345).—The total nitrogen in human urine is dependent on the amount ingested; the relation between urea, uric acid, and xanthine-like substances is also largely a matter of diet. The present paper is devoted to the elucidation of the latter statement.

The analytical data determined were:—(1) total nitrogen; (2) Hüfner nitrogen, that is, the nitrogen of urea and ammonia; the difference between (1) and (2) may be called the nitrogen residue; (3) uric acid *a*, that is, uric acid by Salkowski's method; (4) uric acid *b*, that is, uric acid by Ludwig's method; the difference of the nitrogen of (3) and (4) gives the nitrogen of the xanthine-like substances.

The experiments were made on the author's person, and the following diets were taken for periods of a few days:—A. Pure animal diet. B. Almost pure vegetable diet. C. Vegetarian diet with excess of green vegetables. D. Mixed diet, but without fruit or green vegetables. On some days 1500 c.c. of wine were taken; on others not, but this made practically no difference.

The results are given in full tables; the following abbreviated table gives means only *per diem*:—

Diet.	Total nitrogen.	Hüfner nitrogen.	Nitrogen residue.	Uric acid *a*.	Uric acid *b*.	Nitrogen of xanthine-like compounds.
A......	17·85	16·66	1·19	743	693	17·6
B......	8·61	7·48	1·13	600	508	30·7
C......	7·73	6·63	1·10	539	397	47·3
D......	13·42	11·85	1·57	712	603	36·4

The absolute nitrogen residue is thus almost independent of the amount of proteïd taken in; but the relative nitrogen residue is greater with the smaller ingestion of proteïd. The nitrogen of xanthine-like substances is almost independent of the total nitrogen, and is especially increased by vegetable, and particularly by green vegetable, diet.

A number of analyses are also given contrasting summer and winter urine and male and female urine. The differences are all explicable on the very reasonable assumption that more fruit and green vegetables are eaten in the summer than in the winter, and more by women than by men. The xanthine substances are apparently formed at the expense of the uric acid.

The paper concludes with statistics on the relation of the nitrogen residue to urea, and criticisms on methods of analysis.

W. D. H.

Urobilin in Various Diseases. By G. Hoppe-Seyler (*Virchow's Archiv*, **124**, 30—47).—For comparative purposes, the amount of urobilin in urine may be estimated in the following way:—100 c.c. of urine is acidified with dilute sulphuric acid, and then saturated with ammonium sulphate. This salt precipitates all the urobilin. The red flocculi are collected on a filter, washed with concentrated ammonium sulphate solution, and extracted with equal parts of alcohol and chloroform in a flask, filtered, and the residue is then again extracted with the alcohol and chloroform; water is added to the extract until the chloroform separates. The chloroform solution is then evaporated in a weighed beaker over the water-bath, dried at 100°, extracted with ether, and filtered; the residue is again dissolved in alcohol, placed again in the beaker, evaporated, dried, and weighed.

The urobilin in the urine is increased by:—

(1.) Stasis of the bile in the liver, provided bile can pass into the intestine, and diuresis occurs, as in polycholia.

(2.) Stagnation of the contents of the large intestine, not of the small intestine.

(3.) Hæmorrhages into internal organs.

Approximately the normal amount is found in:—

(1.) Pernicious anæmia.

(2.) Leukæmia and pseudoleukæmia.

It is diminished in:—

(1.) The suspension of hepatic activity that occurs in cachexia, inanition, and many forms of anæmia.

(2.) Stasis of bile in the liver if bile does not pass into the intestine and no diuresis is produced.

(3.) In the course of jaundice, sometimes. The amount of fæcal pigment is no gauge of the amount of urobilin in the urine.

The table given comprises particulars of 55 cases of various diseases, which are compared with 8 normal specimens. The normal mean amounts to 0·123 gram in the 24 hours. W. D. H.

Note by Abstractor.—A good deal of interest attaches to the amount of urobilin in pernicious anæmia. In the single case examined in this research, the amount calculated as being present in the 24 hours' urine is 0·107 gram. One cannot safely draw general conclusions from a single case (compare Abstr., 1888, 1324; 1890, 400, 1017, 1177). W. D. H.

Hæmatoporphyrinuria. By W. D. Halliburton (*Proc. Physiol. Soc.*, 1891, 21).—A case similar to those recently described (this vol., p. 601). It occurred in a woman suffering from melancholia, and who had been taking sulphonal for five months. The high-coloured urine had, however, only lasted for seven weeks. W. D. H.

Rhinoliths. By A. Berlioz (*J. Pharm.*, **23**, 447—449).—Analyses of four rhinolithic calculi:—No. 1, the largest, had a wrinkled surface stained with black blood; the nucleus a cherry stone. No. 2 had a uniform brownish-black surface colour, and was pitted, but contained no nucleus. The third had a peculiar conical shape, with a kind of stalk attached to its base; its colour was whitish-yellow, and was without nucleus. The fourth resembled the second. They were all very hard and gave a smooth fracture. Their concentric layers had a greyish tint. Heated on platinum foil, they left an abundant residue, which was slightly blue in the case of Nos. 2 and 4. Their composition was as follows:—

	1.	2.	3.	4.	
Weight of the calculus ..	3·75	1·34	0·63	0·95	grams.
Water	5·80	5·10	4·0	6·90	per cent.
Organic matter..........	16·60	18·20	16·0	18·10	,,
Calcium phosphate.......	62·02	60·61	61·40	47·63	,,
Magnesium phosphate....	5·08	6·28	3·93	6·68	,,
Calcium carbonate	10·50	9·81	14·67	20·69	,,
Iron...................	?	traces	?	traces	

J. T.

Chemical Constitution and Physiological Action. By T. L. Brunton and J. T. Cash (*Proc. Roy. Soc.*, **49**, 311—314).—In continuation of former work, the present research is occupied with (1) the physiological action of benzene, and (2) the alterations which occur in its action when one or more hydrogen atoms are replaced by (*a*) haloïd radicles, (*b*) alcohol radicles, (*c*) by hydroxyl, (*d*) by NO_2, and (*e*) by NH_2. The modifications produced by changes of temperature were also noticed.

The action of benzene and its compounds is chiefly exerted on the spinal cord, although they act also on the cerebrum, and, to a slight extent, on nerves and muscle. The effect on muscle and nerve is to weaken them, the paralysing action being stronger on the nerve than on the muscle. Their action on the cerebrum is evidenced by lethargy, both in frogs and rats. There is increased excitability of the spinal cord, there being greater diffusion of stimuli with diminished power and definitiveness of movement. Large doses, however, cause paralysis.

Haloïd radicles do not modify the action of benzene to the same extent as they do that of ammonia, but they do so in somewhat the same direction. Monochlorobenzene affects the cord more than benzene, causing spasm and rapid diminution of reflexes. It also weakens the circulation, but does not seem to affect muscles, or motor nerves, more than benzene. The bromo- and iodo-compounds act more powerfully on the cerebrum, and the iodo-compound has a special tendency to paralyse motor nerves, muscles, and cerebral reflexes, and to depress the heart. Heat accelerates, and cold retards, the action of these substances.

The substitution of alcohol radicles for hydrogen in benzene has the effect which one would expect, in having a more sedative action on the nervous system. The circulation is little affected, and their action is more fleeting than is the case with the halogen compounds.

Substitution of hydrogen by hydroxyl increases the tendency to convulsions; this is due to action on the spinal cord.

Amidobenzene produces symptoms resembling those caused by ammonia, consisting in a tendency to produce violent spasm and great paralysis of muscle and nerve. It differs from ammonia in the fact that the convulsions never assume the form of true tetanus.

Nitrobenzene causes lethargy, with increasing tremor or movement, and early abolition of reflex action.

The general action of these compounds on reflex time is to lengthen it, but a primary shortening was frequently observed in the case of chlorobenzene, slightly also in that of methylbenzene, dimethylbenzene, and ethylbenzene.

In producing muscular rigor, chlorobenzene is more powerful than the bromo- and iodo-compounds, and is intermediate in effect between methylbenzene and dimethylbenzene. Of the methylbenzenes, the methyl- is the strongest, the dimethyl- next, and the trimethyl- weakest. Ethylbenzene is of nearly the same strength as methylbenzene in this respect.

In warm blooded animals (cats), respiration is early affected, there being a primary acceleration followed by slowing. The heart stops before respiration in poisoning by benzene and its haloïd compounds, by ethylbenzene, amidobenzene, and nitrobenzene, whilst respiration ceases first in poisoning by the methylbenzenes and hydroxybenzenes.

The first effect of the benzene compounds on the pulse and blood pressure is a quickening and rise respectively; this is followed by a slowing and a fall. W. D. H.

Action of Related Compounds on Animals. By W. Gibbs and E. T. Reichert (*Amer. Chem. J.*, **13**, 289—307; compare Abstr., 1890, 280, 813, and 1018).—*The Hydrazines.*—Phenylhydrazine hydrochloride depresses the cerebro-spinal centres, producing, in the frog, decreased sensibility and voluntary and reflex inactivity, merging into unconsciousness and paralysis. Death results from respiratory and cardiac failure, and the heart stops in diastole. In the dog, it acts at once on the heart, causing a preliminary quickening of pulse and lowering of blood pressure. The hæmoglobin is changed into an abnormal form, the blood becoming almost black. The temperature falls 1—2°. The respiration is at first quickened and then slowed, either by the action of the drug on the respiratory centres, or by the deficient oxygenation of the blood. The action of ortho- and paratolylhydrazine hydrochloride is similar, but less pronounced. The fatal dose, when injected into the jugular vein of the dog, is 0·12 gram of phenylhydrazine hydrochloride, or 0·2 gram of orthotolylhydrazine hydrochloride, per kilo. of body weight.

Toluylenediamine produces in the frog general muscular depression, but does not appreciably affect the sensory and motor nerves. The heart stops in diastole. Administered to the dog, it causes muscular depression, lowering of temperature, salivation, darkening of the blood, and diminution of the rate of respiration. The heart stops in diastole, and the stomach and intestines are found to be congested after death. Small doses of 0·8 gram per kilo., injected intravenously, increase the pulse rate, blood pressure, and respiration rate; the variation in the last is caused by direct action on the respiratory centres. The fatal dose for dogs is 0·2 gram per kilo. when injected subcutaneously; much larger doses may, however, be injected intravenously.

Nitrophenols.—Dinitrophenol injected into the jugular vein of the dog in small doses of 0·2 gram per kilo. causes a stimulation of the vagus, proportional to the amount injected, and a rise in pulse rate and blood pressure. With larger doses (0·17 gram per kilo.), the heart stops before respiration ceases, and the blood pressure falls just before death. The minimum fatal dose is 0·05 gram per kilo. injected. When given by the mouth, the respiration rate at first rises, but subsequently falls, the temperature rises 2—3°, and the pulse rate first diminishes and then increases. The drug seems to act directly on the motor portion of the spinal cord. Death results from respiratory failure when the poison is slowly absorbed through the stomach, from cardiac failure when it passes in mass into the heart. Administered to the frog, dinitrophenol causes muscular depression, stops respiration, and discolours the blood, but the heart continues to beat for a long time after all other signs of life have disappeared. Trinitrophenol injected into the jugular vein of the dog stimulates the pneumogastric nerve or centres to such a degree as to cause the immediate stoppage of the heart. If the pneumogastric nerve is divided, death occurs from respiratory failure. The fatal dose is 0·06 gram per kilo. With the frog, the effect of progressively increasing doses is to stimulate a reflex activity, depress the heart, and stop the respiration. The fatal dose is 0·015 gram per kilo.

Nitrobenzenes.—Nitrobenzene acts on the spinal cord, causing in the frog increase in reflex activity, decrease in voluntary activity, and successive increase and decrease in pulse and respiration rates. The colour of the blood is changed to chocolate, the hæmoglobin being converted into nitrite-hæmoglobin. In the dog, when administered by the mouth, it produces salivation, unsteadiness of gait, rise of temperature and pulse rate, weakness, and unconsciousness; the respiration is quickened by a direct action on the respiratory centres. The animal may recover if the dose does not exceed 0·75 gram per kilo. When injected into the jugular vein, in which case the fatal dose is 0·15 gram per kilo., the blood pressure is diminished by the depression of the heart muscle and vaso-motor centres. The action of dinitrobenzene is similar, but more energetic.

Amides.—Formamide acts on the spinal cord, a dose of 0·3 gram per kilo. causing in the frog convulsions, paralysis, and death from failure of respiration. Injected into the jugular vein of the dog, it acts on the vaso-motor and respiratory centres, and on the cardio-inhibitory centres in the medulla oblongata, causing the blood pressure to fluctuate below and above the normal, checking the respiration, and slowing the pulse. Successive doses, amounting to 1·5 grams per kilo., permanently lower the blood pressure, and cause death from respiratory paralysis. Small doses (0·5 gram per kilo.) of acetamide introduced into the frog cause general relaxation and check the respiration; fatal doses (2 grams per kilo.) in addition increase the reflex activity and produce convulsions of spinal origin. When injected into the dog, the blood pressure is raised, and the rate of respiration is increased, whilst the pulse rate is diminished by the action of the cardio-inhibitory centres. Large doses (up to 5 grams per kilo.) may be injected with immunity, but these, after a time, cause extreme drowsiness and sleep. Propionamide introduced into the frog in doses of 0·5 gram per kilo. diminishes voluntary activity, and causes tetanic convulsions of spinal origin, followed by death. In the dog the effect is small; doses of 0·25 gram per kilo. strengthen the beat of the heart, lower the blood pressure, and act on the cardio-inhibitory centres, checking the pulse. Benzamide diminishes sensibility and reflex and voluntary activity in the frog. The fatal dose is 1·0 gram per kilo. Administered to the dog, it produces the additional effects of staggering, salivation, lowered temperature (1—3°), quickened respiration, and lessened pulse rate. Death results from failure of respiration. Injected into the jugular vein, it causes a rapid fall and rise in the blood pressure, but after repeated doses the pressure does not recover, and the heart is paralysed. The heart beat is lessened in force, the pulse becomes more frequent, and the respiration fails; at the same time, the pupils become dilated and sensibility is destroyed. The fatal dose is 0·5 gram per kilo. Oxamide, thiocarbamide, and pyromucamide have no appreciable effect on the dog.

Anilides.—Formanilide in the frog causes loss of sensibility and reflex and voluntary activity, muscular tremblings, convulsions of spinal origin, paralysis, and death. Administered to the dog by the mouth or subcutaneously in doses of 0·4 gram per kilo., it acts on the respiratory centres, quickening the respiration; on the cardio-inhibitory centres and heart, successively raising and lowering the pulse rate; and on the vaso-motor centres, lowering the blood pressure; it lowers the temperature, increases reflex activity, and produces feebleness and coma, and death from respiratory failure. Acetanilide given to the dog causes vomiting, weakness, lowering of temperature, quickening of pulse, darkening of blood due to formation of methæmoglobin, and cessation of respiration. When injected into the circulation, it acts on the heart, reducing the blood pressure and successively quickening and slowing the pulse. The rate of respiration at first increases, but ultimately diminishes and fails, causing death. The fatal dose is 0·3 gram per kilo. Benzanilide injected into the jugular vein of the dog at first increases the blood pressure, but after the administration of several doses diminishes it. It also quickens the respiration and lowers the temperature. It is probable that the action of the drug is due to mechanical clogging of the capillaries of the nerve centres by the deposition of fine crystals, since enormous doses may be taken into the stomach without any appreciable effect. JN. W.

Tuberculin. By W. HUNTER (*Brit. Med. J.*, ii, 1891, 169—176).—Koch's tuberculin was subjected to approximate analysis with the following results. In order of importance and amount the substances present are :—

(1.) Albumoses: chiefly proto-albumose and deutero-albumose, along with hetero-albumose, and occasionally a trace of dysalbumose. (2.) Alkaloïdal substances, two of which can be obtained in the form of platinochlorides. (3.) Extractives, small in quantity and of unrecognised nature. (4.) Mucin. (5.) Inorganic salts. (6.) Glycerol and colouring matter. Serum albumin, globulin, and peptone are absent.

With regard to its action the following conclusions are drawn :—

1. Tuberculin owes its activity to at least three, and probably more, different substances.

2. Its remedial and inflammatory actions are connected with the presence of certain of its albumoses, whilst its fever producing properties are chiefly associated with substances of a non-albuminous nature.

3. The albumoses are not lost by dialysis; the latter are. It is thus possible to remove the substances which produce fever, while retaining those which are beneficial in their action. The fever is thus not essential to its remedial action, and the same may probably be said for the inflammation, although, under certain conditions, inflammation appears to be beneficial.

4. The remedial action consists in shrinking of the tuberculous tissues, and increased scaling, due to deep local congestions.

5. The remedial substance resists high temperatures. Its action is, however, lessened by a dry heat of 70°. Its properties are materially altered by changes occurring during its purification by dialysis, and thus its preparation is attended with difficulty.

6. The remedial substance and the other albumoses present are stated to belong to the class of "proteïns," that is, albuminous substances derived from the protoplasm of the bacilli themselves, and not merely formed by the action of these bacilli on the surrounding tissues.

Various modifications of tuberculin were prepared, and lettered as follows :—

Modification A contains the total precipitate thrown down by absolute alcohol; it thus contains chiefly albumoses.

Modification C contains all the constituents of tuberculin not present in A.

Modification B contains the whole of the albumoses precipitated by the use of ammonium sulphate, the salt being subsequently removed by dialysis.

Modification CB was prepared from C, and contains the small amount of albumose which was not thrown down by the first precipitation with absolute alcohol. Salts were got rid of by dialysis. Koch is in error when he states that the remedial substance in tuberculin is easily diffusible. This modification is apparently the most satisfactory obtained, as it produces distinct local improvement, unattended with fever, and very little inflammatory action.

These modifications have been chiefly tested on cases of lupus. Further details respecting their therapeutic value are promised.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

New Fermentation of Starch. By SCLAVO and GOSIO (*Bied. Centr.*, **20**, 419; from *Arch. ital. Biol.*, **14**).—Starch paste which had been kept for four months and had decomposed acquired an agreeable, fruity odour, due to the presence of alkyl butyrates, and subsequently an odour of valeric acid was perceptible. This starch paste was found to have the power of inducing the same change in other starch paste. The cause of this change is a bacillus (*Bacillus suaveolens*), which was isolated. The bacillus has no pathogenic properties, will develop on all the usual nutritive solutions, and presents a characteristic appearance in plate cultures; it does not liquefy gelatin. In order to develop spores, the bacillus requires air and a temperature of 22—29°, and a nutritive substance as neutral as possible. Acid is then produced to a certain limit (corresponding with 0·0676 per cent. of potash), when no more is formed. A trace of nitrogen is necessary for the nourishment of the bacillus. In milk, broth, hay extract, and aqueous extracts of straw and beetroot, the bacillus produces the same odour. It converts starch gradually into dextrin and glucose with formation of alcohol, aldehyde, formic, acetic, and butyric acids, together with ethereal substances of an agreeable odour.

N. H. M.

Fat and Ethereal Oil of Sabadilla Seeds. By E. OPITZ (*Arch. Pharm.*, **229**, 265—289).—The seeds, when extracted with light petroleum, yield a fat which is obtained on distillation of the extract in a vacuum as a greenish-brown liquid, easily soluble in alcohol, ether, and benzene; sp. gr. 0·953. It is neutral to test-paper, and is approximately composed of oleïc acid 50 per cent., palmitic acid 36·3, cholesterol 4·12, and glycerol 9·55 per cent. The fat, distilled in a current of steam, yields a small quantity of an ethereal oil, containing ethyl and methyl salts of veratric and hydroxymyristic acids, aldehydes of the lower fatty acids, and high-boiling polyterpenes. The volatile fatty acid described by Pelletier and Caventou could not be detected.

J. T.

Fats of Amanita pantherina and Boletus luridus. By E. OPITZ (*Arch. Pharm.*, **229**, 290—292).—These fungi yield a considerable amount of fatty oil when extracted with ether. After a short time the oil deposits phytosterol crystals; when freed from these, the fatty material has a thick, oily consistence and a dark-brown colour. Half of the mass consists of free fatty acids. Both fats contained oleïc and palmitic acids, glycerol, and phytosterol. J. T.

Proteïds of the Oat-kernel. By T. B. OSBORNE (*Amer. Chem. J.*, **13**, 327—347).—By concentrating the hot alcoholic extract of freshly-ground oats and treating the residue with alcohol and ether, several fractional precipitates were thrown down containing from 6 to 13·92 per cent. of nitrogen. These fractions, on further treatment, yielded four portions of a coagulated proteïd having the mean composition C, 52·96; H, 6·9: N, 16·4; O, 23·74.

A proteïd soluble in alcohol was of practically identical composition and contained 2·25 per cent. of sulphur.

The alcoholic extract from oats which had been previously extracted with water yielded an uncoagulated proteïd containing C, 53·64; H, 6·88; N, 15·70; S, 1·75.

When 10 per cent. sodium chloride solution was substituted for the water, two portions of uncoagulated proteïd were obtained of the composition C, 53·97; H, 6·97; N, 15·66; S, 1·80; O, 21·60.

When the water and salt solution were applied in succession, the uncoagulated proteïd extracted by alcohol contained C, 53·63; H, 7·16; N, 15·83; S, 1·74; O, 21·64.

Two distinct proteïds can thus be obtained from oats (compare Kreusler, *J. pr. Chem.*, **107**, 17). That extracted from untreated oats readily coagulates and becomes insoluble in alcohol, and when wet with absolute alcohol does not absorb moisture from the air; whilst that obtained from oats after treatment with water or salt solution has no tendency to coagulate, is freely soluble in cold alcohol of 0·9 sp. gr., and when wet with absolute alcohol absorbs moisture from the air and becomes gummy. Both substances, when washed with absolute alcohol and dried, are light yellowish powders, soluble in dilute acids and alkalis and reprecipitated on neutralising their solutions. JN. W.

Development of Wheat, and Formation of Starch in the Grain. By HÉBERT (*Ann. Agron.*, **17**, 97—115).—The author has studied the development of the wheat plant in the light of the recent knowledge obtained as to the composition of straw. Dehérain has shown that much of the undetermined matter in the ordinary analysis of straw consist of vasculose; Wheeler and Tollens, that the saccharifiable substance present in straw is not starch but straw gum, analogous to wood gum, giving by treatment with acids a reducing sugar called xylose; and the author (*Ann. Agron.*, **16**, 358) has based on these discoveries a new method for the analysis of straw.

The following table shows the composition of Bordeaux wheat grown at Grignon in 1890, at the different times of sampling :—

Composition of dry matter.	May 13.	June 8.	July 2.		July 16. Stems.
			Stems.	Heads.	
Ash	14·95	11·68	9·26	5·93	12·19
Nitrogenous matter (N × 6·25)	21·66	9·81	5·31	9·85	6·72
Fat and chlorophyll	3·50	2·14	1·93	2·61	1·88
Substances soluble in water (ash deducted)—					
Reducing sugars	6·56	4·99	2·89	1·92	2·69
Non-reducing sugars	5·01	6·15	3·64	2·57	3·87
Gums, tannins, &c.	none	0·58	8·53	4·57	7·68
Cellulose	20·18	23·48	26·32	22·93	27·46
Vasculose	9·03	16·39	13·07	13·23	13·73
Straw gum (reckoned as xylose)	18·28	26·93	30·51	30·50	25·53
Starch	—	—	—	6·22	—
	99·16	102·15	101·46	100·33	101·74

The ears of grain had by July 16 lost so much by attacks of birds that no analysis was made. The kilograms *per hectare* of the various ingredients contained in the plant at the different dates are given in the next table.

	May 13.	June 8.	July 2.			July 16. Stems.
			Stems.	Heads.	Total.	
Ash	174	553	573	122	695	1260
Nitrogenous substances	252	465	328	203	531	695
Fat and chlorophyll	41	101	119	54	173	194
Reducing sugars	76	236	179	40	219	278
Non-reducing sugars	58	291	225	53	278	400
Gums, tannins, &c.	—	27	528	94	622	794
Cellulose	234	1113	1628	473	2101	2839
Vasculose	105	777	808	273	1081	1419
Straw gum = xylose	212	1276	1887	629	2516	2638
Starch	—	—	—	128	128	—

These results throw some light on the source of the starch in the grain. The straw gum, really contained in the stems instead of the starch or amylaceous substance formerly supposed to accumulate there ready for transportation to the grain, does not appear to be the source. It increases in the straw regularly up to the end of maturation, forming 25—35 per cent. of ripe straw, is insoluble in water, difficultly attacked by acids, and requires a long time for transformation into xylose.

To throw more light on the point, analyses were made of different samples of grain (from another district) at different periods of ripening, viz., July 15 and 23; the detailed analyses are given in the paper. At the earlier period the grain contains about 10 per cent. of reducing sugar. A solution of this sugar heated with phenylhydrazine acetate gave an osazone melting about 210°, which nearly corresponds with the melting point of phenylglucosazone; the sugar should be glucose or levulose, probably glucose. The non-reducing soluble carbohydrate in the grain on July 15 gives the reactions of a dextrin; a search for saccharose gave a negative result. The non-reducing substance in the young stems appears to be dextrin also, so there is reason for supposing that the glucose and dextrin of the early grain are both simply transported from the stems. In the ripe grain no glucose is found, and it is, in all probability, one of the substances transformed into starch. It is certain that the starch is not formed early in the life of the plant and then transported, and it is equally certain that it is not formed by chlorophyll action during the maturation, for at that period the leaves are yellow and withered.

As to the nitrogenous matters, the author's results confirm those of Pierre, which showed an accumulation in the straw and subsequent migration into the grain. J. M. H. M.

Formation of Phlobaphenes. By A. TSCHIRCH (*Chem. Centr.*, 1891, i, 583; from *Schweiz. Wochenschr. Pharm.*, **29**, 62—64).—With few exceptions, the tannins are found dissolved in the cell sap and are oxidised either directly or, in the event of their being present in the form of glucosides, after resolution into their constituents, to red-brown phlobaphenes. To this class of compounds belong quina red, tormentilla red, filix red, ratanlica red, illicium red, nelken red, cinnamon red, kino red, catechu red, &c. The tannins of the oak and sumach (*Rhus coriaria*) as well as the majority of the pathological tannins are either not oxidised at all or but very slowly, and phlobaphenes are not formed. The formation of filix red takes place very slowly, whilst that of quina red is very rapid, and in the case of the tannin in *Cinchona succirubra* the author has observed the change take place at the end of 15 seconds. The behaviour of the tannins when subjected to heat varies greatly, some being very stable whilst others are equally sensitive. In the case of tea, if the leaves are allowed to ferment and are then dried, the phlobaphene is formed and the product is black tea, whilst if the leaves are heated directly after gathering, the tannin is destroyed and the phlobaphene is not formed, the product being green. J. W. L.

Changes occurring during Ensilage. By O. KELLNER, Y. KOZAI and Y. MORI (*Landw. Versuchs-Stat.*, **39**, 105—114).—In continuation of former researches, the authors have further examined the changes which occur in the nitrogenous portion of fodders in silage. It appears that when air is excluded the chemical changes do not result in a loss of nitrogen, and when such silage is dried as for analysis, ammonia is lost by dissociation of its organic salts; as much as 23·3 per cent. of the total nitrogen may thus be lost (buckwheat). When nitrates are present (0·21 per cent. nitrogen in turnip leaves), as much as 10·3 per cent. of the total nitrogen may be lost; this corresponds with a quantity more than that which is contained in the fodder as nitrate; consequently it appears that under these conditions other nitrogenous matters are destroyed. but hitherto no explanation can be found for this condition of affairs. Drying silage before estimating its digestibility is not advisable; the proteïds of rye grass, buckwheat, &c., become less digestible after ensiling. E. W. P.

Analytical Chemistry.

Burette-float for Opaque Liquids. By H. Rey (*Ber.*, **24**, 2098).—For opaque liquids, the author recommends the employment of a float with two bulbs, so weighted that the upper and smaller one, which bears the usual horizontal mark, is above the surface of the liquid. The readings may then be obtained with as great accuracy as in the case of transparent liquids. H. G. C.

Estimation of Free Hydrochloric Acid in the presence of Acid Phosphates by means of Calcium Carbonate. By C. Friedheim and H. Leo (*Pflüger's Archiv*, **48**, 614—624).—In a fluid such as the contents of the stomach, where free hydrochloric acid and acid phosphates may occur, the acidity may be estimated in the following way:—Free hydrochloric acid is neutralised by shaking the mixture with powdered calcium carbonate in the cold, carbonic anhydride being given off. The acidity of acid phosphates is not altered by this procedure. If the solution is titrated before and after treatment with calcium carbonate, the amount both of the free acid and of the acid phosphates is obtained. This method, previously published (Leo, *Centr. Med. Wiss.*, 1889, No. 26), has been criticised by various observers (Hoffmann, Wagner), and the present paper is chiefly concerned in answering these criticisms. W. D. H.

Detection of Chlorine and of Chlorides in presence of Bromides and Iodides. By G. Denigès (*Bull. Soc. Chim.* [3], **5**, 66).—In addition to an aqueous solution of aniline for the detection of chlorine as described in a previous communication (this vol., p. 495), the author recommends a solution of phenol (40 grams) and aniline (5 c.c.) in water (1 litre), which yields a beautiful blue coloration in presence of traces of hypochlorite, the reaction not being affected by the presence of traces of bromine. T. G. N.

Detection and Estimation of Iodine in Urine. By A. F. Jolles (*Zeit. anal. Chem.*, **30**, 288—292).—After the internal or external use of iodine compounds, iodine appears in the urine. To detect it qualitatively, 10 c.c. of the urine should be mixed with an equal volume of concentrated hydrochloric acid, and 2 or 3 drops of weak chlorine water run down the side of the test tube. In presence of iodine, at the surface of contact a brown ring is formed, which turns blue on adding starch paste. When compounds of the indigo series are produced by the action of the chlorine, they give a similar ring, but one of much less intensity and situated below and separate from the iodine ring. Should the brown ring fail to turn blue with starch, this is probably due to the use of too much chlorine, and a weaker chlorine water should be tried. The test is very sensitive; 1/500 per cent. is about its lower limit.

The method recommended for estimating the iodine is to char the dry residue of the urine, and precipitate the iodine, together with more or less of the chlorine, by silver nitrate. The amount of silver iodide in the weighed precipitate is then ascertained by fusing part of it in a current of chlorine, and calculating from the loss of weight due to the displacement of iodine by chlorine. M. J. S.

Metaphenylenediamine as a Test for Active Oxygen. By P. Cazeneuve (*J. Pharm.*, **23**, 542—544).—The reagent consists of a 1 per cent. solution of the hydrochloride in 93° alcohol, to which 10 drops of ammonia is added. Contact with air, or the passage of a current of oxygen, only causes a slight bluish-green tint after some hours. Oxygen under a pressure of 300 atmospheres does not colour the reagent. On the contrary, when shaken up with platinum black, or animal charcoal, the liquid takes an indigo tint. All the blacks used for decolorising produce the same colour, and the tint varies with the decolorising power. Hydrogen peroxide gives an intense blue tint in the cold, whilst ozonised oxygen produces a reddish-brown coloration. The reagent thus indicates that the active oxygen in the latter case differs dynamically from the preceding cases. J. T.

Belgian Method of Estimating the Soluble Phosphoric Acid of Superphosphates. By D. Crispo (*Zeit. anal. Chem.*, **30**, 301—303).—It was formerly the practice to treat a weighed quantity of the phosphate with a large volume of water at once, and, after digestion with frequent shaking, to estimate the phosphoric acid in solution. By this treatment, however, the phosphoric acid, the monocalcium phosphate, and the iron and aluminium sulphates attack the undecomposed tricalcic phosphate, forming compounds which are not soluble in feebly acid water, and therefore escape estimation. At a meeting of Belgian chemists held two years ago, the following process was therefore adopted as one resembling more closely that which goes on in the soil:—5 grams of the substance is rubbed dry in a mortar, and then treated with a small quantity of water. After thorough disintegration and subsidence, the solution is decanted through a filter into a half-litre flask. This treatment is repeated, the contents of the filter being each time allowed to drain through before refilling. Finally, the residue is rinsed upon the filter and thoroughly washed. Any turbidity produced in the filtrate by the admixture of the various washings is cleared by the addition of nitric acid, before filling up to the mark and estimating by the molybdate method. M. J. S.

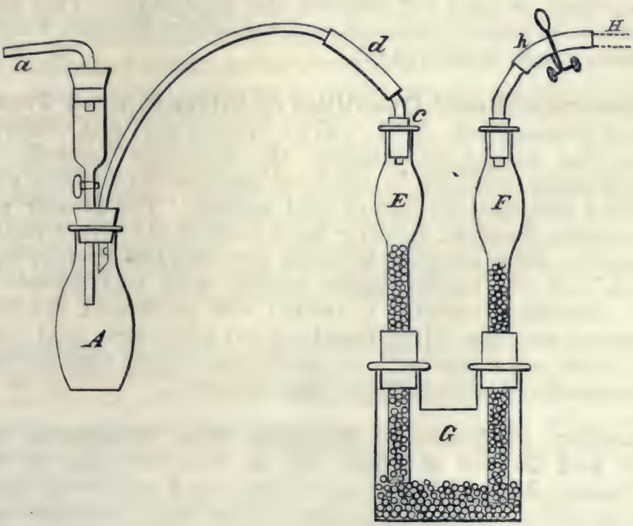
Assay of Ferric Hypophosphite. By F. X. MOERK (*Pharm. J. Trans.*, **21**, 1177).—0·2 gram of finely-powdered ferric hypophosphite, 1·0 gram of citric acid, and 25 c.c. of water are stirred together until the acid dissolves; then dilute ammonia is added gradually in order to decompose the hypophosphite, the ferric hydrate being largely dissolved by the ammonium citrate. The mixture is frequently stirred for 10 minutes more, then 75 c.c. of a cold, saturated solution of mercuric chloride is added, and after that, hydrochloric acid, drop by drop, with constant stirring, until calomel begins to precipitate. The vessel is allowed to stand in the cold for half an hour, and for a further half hour in a water-bath at 100°. The weight of the mercurous chloride precipitated multiplied by 0·088934 gives the weight of the ferric hypophosphite. R. R.

Bettendorf's Arsenic Reaction. By H. WARNECKE (*Chem. Centr.*, 1891, i, 760—761; from *Pharm. Zeit.*, **36**, 167—168).—In place of the stannous chloride solution in hydrochloric acid, prepared according to the *Pharm. Germ.* III, the author prefers dissolving 1 part of crystallised stannous chloride in 2 parts of strongly fuming, 38—40 per cent., hydrochloric acid.

1 c.c. or 1 gram of the substance to be tested is added to 5 c.c. of the tin solution, the reaction being observed for 15 minutes. Calcium phosphate and zinc oxide dissolve to a colourless solution; 1 gram of bismuth subnitrate causes a pale-yellow coloration, whilst 1 c.c. of *liq. ferri sesquichlorat.* causes a weak, greenish coloration. In most cases, the substance under investigation is heated to boiling with the stannous chloride solution, but in the presence of bismuth subnitrate or ferric chloride, the coloration produced by these substances interferes with the arsenic reaction. J. W. L.

Modification of Pettenkofer's Method of Estimating Carbonic Anhydride in Air. By A. LEBEDINZEFF (*Zeit. anal. Chem.*, **30**, 267—279).—The modification consists essentially in protecting the baryta solution completely from contact with unpurified air, or with caoutchouc, at any stage of the work. The baryta store bottle and stopcock burette are connected so as to form a closed system, into which only purified air can enter, and the baryta is measured into thin-walled tubes, of pipette form, previously filled with purified air, which are then sealed before the withdrawal of the burette jet. The air bottle is fitted with a hollow glass stopper, carrying two stopcock tubes. One of the baryta tubes (the total bulk of which must be ascertained) is placed in the dry air bottle before the latter is filled with the air to be analysed. After aspirating through the bottle (which holds 7 to 12 litres) about 200 litres of air, the stopcocks are closed and made air-tight with a mixture of paraffin and wax, the baryta tube is broken, the bottle shaken for half-an-hour, and then left for 24 hours. It is then inverted and connected to a small subsidence bottle (filled with purified air), into which its contents are allowed to flow. The pipette for removing an aliquot portion is inserted through a glass tube, with rubber connector, passing through the caoutchouc stopper, and is then transferred to the titration bottle through a similar tube. The stopper of the titration bottle carries also the oxalic acid burette and a soda-lime tube. All the apparatus is figured, and the various precautions minutely described. For the standard acid, Trommsdorf's "*acidum oxalicum purissimum*" was crystallised seven times from hydrochloric acid, then from water, and air dried. But although dissolved in the proper proportion to correspond with 1 milligram of CO_2 per c.c., its actual value was found by two independent methods to be only 0·9752 milligram. Phenolphthaleïn was used as indicator. Special experiments showed that the baryta solution, whether in the store bottle or in the sealed tubes, underwent no alteration during a month. Blank experiments with purified air indicated 0·128 vol. in 10,000 of air. The estimations made up to the present time have only been for the purpose of testing the method. The results obtained in Odessa and its neighbourhood range from 2·88 to 3·34 vols. per 10,000. M. J. S.

Estimation of Carbonic Anhydride. By F. Tschaplowitz (*Zeit. anal. Chem.*, **30**, 279—282).—The following process is suitable for the estimation of small quantities of carbonates. The substance is decomposed by boiling it with dilute sulphuric acid in the flask *A*, and the carbonic anhydride evolved is absorbed by a measured quantity of potash solution in the vessel *EFG*, which contains glass balls as large as peas. After filling the whole with purified air, there is measured into the bulb *E* 25 c.c. of potash solution of about 1·5 per cent., with enough boiled water to cover the glass balls in *G*. By suction at *a*, whilst *h* is closed, a partial vacuum is produced, and sulphuric acid is then drawn into *A* from the stopcock funnel. When the absorption of the carbonic anhydride is complete, the balls are



rinsed from *E* and *F* into *G* with hot water, and, after adding excess of barium chloride (0·8 to 1·0 gram), closing, shaking, and leaving for two hours, the residual alkaline hydroxide is titrated in the vessel *G* by means of oxalic acid with turmeric indicator. The strength of the original potash is ascertained by a similar titration, and the difference is the amount neutralised by the carbonic acid. Test analyses show results ranging from 1·4 per cent. deficiency to 0·9 per cent. excess.

M. J. S.

Estimation of Lithium in Mineral Waters. By E. WALLER (*Chem. Centr.*, 1891, i, 641; *J. Amer. Chem. Soc.*, **12**, 214—223).—The author has experimented with the methods of Meyer, Gooch, and Carnot for the estimation of lithium.

In converting the alkalis into chlorides, it is to be noted that the barium precipitate (sulphate and carbonate) carries down appreciable quantities of the alkalis, especially lithium, and in order to avoid error the washing must be very thorough, and the barium carbonate should be dissolved and reprecipitated. The liability of lithium chloride to dissociate must also be remembered. In applying Meyer's phosphate method, the chlorides are dissolved in a small and known volume of water, precipitated with excess of disodium phosphate and sodium hydroxide, evaporated to dryness, redissolved in water, an equal volume of concentrated ammonia added, allowed 12 hours to precipitate, and washed with dilute ammonia. Gooch's amyl alcohol method (Abstr., 1887, 528) gives the best results, provided the quantity of chlorides does not amount to more than 0·2 gram. Carnot's fluoride method includes a serious error, the solubility of lithium fluoride being 0·004 gram in 7 c.c. of the ammonia and ammonium fluoride, which is used for washing the precipitate. This washing liquid must be freshly prepared, and any silicon fluoride, which may precipitate, carefully filtered off. J. W. L.

Estimation of Small Quantities of Silver in Lead Flux. By G. HEPPE (*Chem. Centr.*, 1891, i, 470; from *Chem. tech. Centralanz.*, **9**, 11).—The author recommends the following method. From 150—200 grams of the finely powdered lead flux is treated at a gentle heat with a saturated solution of lead acetate. The greater part of the lead oxide dissolves, forming basic acetate, the silver remaining undissolved. After allowing to settle, the clear supernatant liquid is decanted, and the residue again treated with lead acetate. The portion remaining insoluble is treated with acetic acid, the solution concentrated, and the silver dissolved out with nitric acid and estimated in the usual manner. A small quantity of copper is almost always present, and frequently a little bismuth. J. W. L.

Separation of Mercuric Sulphide from Sulphides of the Arsenic and Copper Groups. By K. POLSTORFF and K. BÜLOW (*Arch. Pharm.*, **229**, 292—309).—On digesting a mixture of mercury, lead, silver, bismuth, copper, arsenic, and antimony sulphides with a mixture of equal volumes of potassium sulphide and potassium hydroxide solutions, the sulphides of lead, silver, bismuth, and copper are perfectly insoluble, whilst the sulphides of mercury, arsenic, and antimony are dissolved completely. From this solution the mercury sulphide can be quantitatively separated by warming with ammonium chloride. In the presence of cadmium or tin, the above method is inapplicable. It is convenient to employ a 15 per cent. solution of hydroxide; the sulphide solution is prepared by saturating a measured volume of this solution with hydrogen sulphide, and then adding an equal volume of the hydroxide. The numerical results quoted show the method to be very exact. J. T.

Manganese Ammonium Ferrocyanide. By L. Blum (*Zeit. anal. Chem.*, **30**, 282—283).—On adding potassium ferrocyanide to an ammoniacal solution of a manganous salt in presence of ammonium chloride, the precipitate has the constant composition

$$Mn(NH_4)_2Fe(CN)_6.$$

Consequently, 1 c.c. of a solution containing 38·487 grams of crystallised potassium ferrocyanide in a litre will precipitate 0·005 gram of manganese. The precipitate is not soluble in acetic acid.

M. J. S.

Volumetric Estimation of Manganese. By L. Blum (*Zeit. anal. Chem.*, **30**, 284—288).—Based upon the facts stated in the foregoing abstract, a method can be founded for the titration of manganese in presence of iron, strictly analogous to that of Donath and Hattensauer for zinc (this vol., p. 113; also Abstr., 1887, 183). The manganese solution is mixed with a little ferric chloride, and a large excess of ammonium chloride, tartaric acid, and ammonia, heated to boiling, and titrated with a ferrocyanide solution, the end of the precipitation being shown by bringing a drop in contact with acetic acid on a porcelain plate, when any excess of ferrocyanide produces a blue colour. In coloured solutions, especially such as from the presence of much iron have a strong yellow colour, the indication is by no means sharp. The process is therefore unsuitable for manganiferous iron, but manganese ores generally give a solution which is sufficiently colourless. The presence of zinc, or of ferrous iron, would cause the results to come out too high. The latter may be peroxidised by nitric acid, and the former is rarely present in manganese ores in noteworthy quantity. The ferrocyanide solution must be standardised with known quantities of manganese, since the commercial salt frequently contains sodium, and therefore precipitates more manganese than would be calculated from the equation. M. J. S.

Separation of Ferric Oxide from Alumina. By F. Beilstein and R. Luther (*Chem. Centr.*, 1891, i, 809—810; from *Bull. Acad. St. Pétersbourg*, **13**, 149—158).—The authors take advantage of the insolubility of basic ferric nitrate in solutions of salts, especially ammonium sulphate, and of the solubility of basic aluminium nitrate in such solutions.

If neutral aluminium nitrate be heated on the water-bath until it ceases to lose weight, water and nitric acid are lost, and the basic nitrate, $2Al_2O_3,3N_2O_5,2H_2O$, is formed. This nitrate is readily soluble in water, is not decomposed by heating to boiling, and is not precipitated by ammonium sulphate. If the aqueous solution be *boiled* with ammonium sulphate, a precipitate is formed which redissolves, in part, on cooling, and is free from sulphuric acid. If a solution of normal aluminium nitrate be evaporated to dryness on the water-bath with some ammonium nitrate, the formation of the basic nitrate is not interfered with.

Normal ferric nitrate, if heated on the water-bath, loses water and nitric acid with formation of several basic nitrates of varying composition. They vary in colour from yellow to red and brown, and partly dissolve in water to a muddy, dark-red liquid. The solution proceeds more rapidly in hot than in cold water, but the solution is muddier, and passes through a filter still muddy, the solution not becoming clear even if left for several weeks. The iron is present in the colloïdal state, and is precipitated by the addition of a few drops of ammonium, sodium, or copper sulphate. Water dissolves the precipitate somewhat, but it is quite insoluble in solutions of salts. It is readily soluble in hydrochloric acid, less soluble in nitric acid, and still less in sulphuric acid. By evaporating normal ferric nitrate with ammonium nitrate, similar basic nitrates are obtained.

For the separation of the two oxides, the solution in nitric acid is evaporated to dryness and heated on the water-bath until acid ceases to be evolved. The residue is treated with hot water, broken up carefully, and boiled for 10 minutes. After cooling, 2—3 c.c. of 10 per cent. ammonium sulphate solution is added, the precipitate allowed to settle, and then filtered. The filtration proceeds slowly through paper, and a layer of fine asbestos on a platinum cone will be found better. The precipitate is washed with cold, and finally with hot, ammonium sulphate solution. The first portions of the filtrate are frequently not quite clear, and it is recommended to pass this through the filter a second time. A little alumina is frequently precipitated with the ferric nitrate, but this may be entirely separated by dissolving the latter in dilute nitric acid and reprecipitating the basic ferric nitrate. The results obtained are satisfactory.

J. W. L.

Decomposition of Chrome Iron Ore by Means of the Electric Current. By E. F. Smith (*Ber.*, **24**, 2182—2185).—The chromium in chrome iron ore can be rapidly and accurately estimated by the following process, which is based on the fact that when an electric current is passed through a fused mixture of potash and chrome iron ore, the chromic oxide is completely converted into potassium chromate.

Caustic potash (30—40 grams) is melted in a nickel crucible placed on a thick copper-wire ring, which is connected with the anode of a battery; the finely divided mineral (0·1—0·5 gram) is carefully added, and then a platinum rod, connected with the cathode of the battery, is introduced into the fused mass through a hole in a watch-glass, placed over the crucible. A current of not more than 1 ampère is then passed for at least 30—40 minutes, but before finally breaking the current, it is reversed for a short time, in order to bring about the oxidation of particles of the mineral which are enclosed in the iron deposited on the cathode. The contents of the crucible are then digested with water, the solution filtered, the residue washed well with boiling water, and the chromium, which is present in the filtered solution as potassium chromate, estimated either gravimetrically or volumetrically by the usual methods; the portion insoluble in water should be completely soluble in warm hydrochloric acid, otherwise the mineral has not been completely decomposed.

Quantitative experiments gave concordant results, which agreed with those obtained by Dittmar's and by Genth's method for the analysis of chrome iron ore. F. S. K.

Detection and Estimation of Titanium. By A. NOYES (*Chem. Centr.*, 1891, i, 812; from *J. anal. Chem.*, **5**, 39).—0·1 gram of the finely pulverised mineral is fused with 0·2 gram of sodium fluoride and 3 grams of sodium hydrogen sulphate; the flux is treated with 15—20 c.c. of water, filtered, and washed, so that the total volume of liquid does not exceed 30 c.c. The titanium is then determined colorimetrically by comparing the coloration produced by hydrogen dioxide with that obtained with a solution containing a known amount of titanium. The presence of iron interferes somewhat with the determination. The difficulty may be obviated by adding to the standard solution of titanium as much ferric sulphate as will produce the same coloration as the iron in the solution under examination. The strength of coloration produced by the hydrogen peroxide with the titanium may now be measured. If the test is only to be a qualitative one, the solution is divided into two parts and hydrogen dioxide added to one, the yellow colour produced by any titanium being then readily detected. J. W. L.

Solubility of Thallium Iodide and Estimation of Thallium. By J. H. LONG (*Zeit. anal. Chem.*, **30**, 342—344; from *J. anal. Chem.*, **2**, 243).—One part of thallium iodide requires for solution 17,000 parts of water at 20°, but when the salt is simply washed with water on a filter, somewhat more water is required. Of 90 per cent. alcohol, 260,000 parts are required: when washing with alcohol on a filter, 1 part dissolved in 500,000. With 50 per cent. alcohol, 1 part dissolved in 37,000 parts on digestion; in 51,000 on washing. In ammonia, whether of 6·5 per cent. or of 2·5 per cent., the same solubility of 1 in 13,000 was found. Ammonia of 1·25 per cent. gave the same solubility as water. In a 10 per cent. solution of potassium iodide, thallium iodide seems quite insoluble, and, even in a weaker solution the solubility is very small. The process recommended for estimation is as follows:—A small excess of potassium iodide is added to the warm concentrated solution of the thallium salt. After complete cooling, the thallium iodide is filtered off by a Gooch filter, washed with 50 per cent. alcohol, and weighed after drying. A correction may be made for the amount dissolved by the alcohol.

M. J. S.

Separation and Estimation of Antimony. By J. THIELE (*Annalen*, **263**, 361—376).—The method of separating tin and antimony, based on the precipitation of the latter from the solution of the chlorides with metallic iron, is not an exact process; in washing the precipitated metal, even when the water has been previously boiled, a considerable quantity of antimony passes into solution; the metal also undergoes oxidation to such an extent that, in spite of the loss experienced in washing, the results sometimes come out too high.

Antimony pentasulphide, obtained by precipitating an antimony solution with hydrogen sulphide, and then washing with carbon bisulphide in the usual way, is invariably impure; when antimony is estimated as pentasulphide, the results obtained are too low.

The author has made a number of experiments, the details of which are given, in order to determine the magnitude of the errors in the two methods of estimating antimony just referred to. F. S. K.

Electrolytic Separations. By E. F. SMITH and F. MUHR (*Ber.*, **24**, 2175—2181; compare *Amer. Chem. J.*, **12**, 252; and *J. Frank. Inst.*, **129**, 239; **131**, 300).—Gold can be completely deposited from a solution of potassium aurocyanide by means of the electric current; the deposition of palladium, on the other hand, from a solution containing excess of potassium cyanide, does not begin until a current of $\frac{1}{100}$ ampère has been passed for 36 hours. This difference in behaviour can be made use of for the separation of the two metals; employing dilute solutions and a current of suitable strength (0·4 to 1 c.c. of electrolytic gas per minute), the complete separation of the gold requires from 12 to 14 hours, and the deposited metal is free from palladium.

Gold can also be separated from platinum, copper, cobalt, nickel, and zinc in a similar manner; but in the case of zinc, the current strength must be at least 2—3 c.c. of electrolytic gas per minute.

The results of numerous experiments showed that the quantity of gold obtained in this way is, in the majority of cases, in excess of the theoretical, sometimes as much as 0·63 per cent.

When a solution of silver and platinum in excess of potassium cyanide is electrolysed with a current strength equal to 1 c.c. of electrolytic gas per minute, the deposited silver is free from platinum; mercury can be separated from platinum under the same conditions, employing a current equal to 0·2 c.c. of electrolytic gas per minute, but the separation of cadmium and platinum cannot be completely effected. F. S. K.

Action of Hydriodic Acid on Substances containing Sulphur. By R. BENEDIKT and M. BAMBERGER (*Monatsh.*, **12**, 1—4).—Zeisel has previously observed (Abstr., 1886, 1079) that the method of estimating methoxyl by boiling the substance with hydriodic acid and determining, as silver iodide, the methyl iodide evolved is not available in the case of some compounds which contain sulphur, because the silver iodide is contaminated with sulphide, and, when an attempt is made to expel hydrogen sulphide, the weight of the silver iodide remaining falls below that required by theory. The authors have experimented with the object of ascertaining whether the presence of sulphur invariably interferes with the estimation of methoxyl by this method. In their investigations, they made use of

Benedikt and Grüssner's apparatus, the bulb of which was filled with a 10 per cent. solution of cadmium iodide and red phosphorus, whereby the hydrogen sulphide was almost entirely retained. The traces of silver sulphide sometimes contained in the precipitate were removed by gentle warming with dilute nitric acid. The following results were obtained:—(1) Potassium methyl sulphate, $KMeSO_4 + \frac{1}{2}H_2O$, gave, on boiling with hydriodic acid, too little methyl iodide and a considerable separation of sulphur. When, to the hydriodic acid, a little red phosphorus was added, a loss of methyl iodide occurred, and this loss seemed to be due to the formation of mercaptan, a substance which, in the form of mercury mercaptide, was found to be unattacked when boiled with hydriodic acid of sp. gr. 1·70. (2) Potassium sulphate was reduced by hydriodic acid to sulphur and hydrogen sulphide, and by hydrogen iodide and red phosphorus to sulphur. (3) Free sulphuric acid was acted on by hydriodic acid in precisely the same way as potassium sulphate. (4) Potassium paraphenolsulphonate gave rise to much sulphur and hydrogen sulphide, and was completely reduced to phenol. (5) The presence of substances containing sulphur, such as potassium sulphate, led to the production of too little methyl iodide when nitroeugenol was boiled with hydriodic acid and red phosphorus.

G. T. M.

Estimation of Uric Acid in Urine. By J. B. HAYCRAFT (*Brit. Med. J.*, ii, 1891, 10; *Proc. Roy. Soc. Edin.*, **18**, 255—258; and *Zeit. physiol. Chem.*, **15**, 436—455).—The author's method of estimating uric acid in urine (*Brit. Med. J.*, ii, 1885) has been adversely criticised by Gossage (Abstr., 1889, 450) and Salkowski (*ibid.*, 1250), and favourably noticed by Herrmann (Abstr., 1888, 1225) and Czapek (*ibid.*). Salkowski alleges that there is no constancy in the amount of silver in silver urate, and quotes twelve analyses which support this view. In the present contribution to the discussion, it is alleged that errors are present in Salkowski's tables, which, when corrected, place his results in accord with those of Haycraft. What they prove is that, by his method, Salkowski finds about 14 milligrams less uric acid than by the silver process. The ratio between the silver and uric acid appears inconstant, because in weak urines a loss of 14 milligrams will be comparatively heavy, whilst in stronger urines the loss will be less felt. This constant difference is due, in part, to imperfections of Salkowski's own method, but the mere existence of the constant difference is stated to prove the proposition that silver urate has a constant composition. This difference has been reduced to within the limits of manipulative error by Herrmann and Czapek.

W. D. H.

Estimation of Ash in Raw Sugar. By A. STIFT (*Chem. Centr.*, 1891, i, 445; from *Öster.-ungar. Zeit. Zück. Ind.*, **19**, 484—489).—Having used von Grobert's method of burning the ash of raw sugars and sugar liquors with the aid of oxalic acid, the author finds that the results obtained coincide with those obtained by burning the ash alone. He finds, however, that the proportion of oxalic acid required is, in most cases, very considerable, from twice the weight of the sugar in the case of raw sugars to five times the weight of substance in the case of molasses. To use less oxalic acid by sprinkling some more upon parts of the ash which have not burnt perfectly has not proved, in the author's hands, an altogether successful modification.

J. W. L.

Estimation of Sugars with Potasssium Cuprocarbonate Solution. By H. Ost (*Ber.*, **24**, 1634—1636; compare this vol., p. 125).—These determinations were conducted in a manner similar to those already published; the maltose solutions were boiled for 10 minutes before collecting the cuprous oxide; as with other sugars, less attention to details is needed than is required by the use of Fehling's solution. The following table embodies the results:—

Copper.	Maltose hydrate.	Maltose, anhydrous.	Copper.	Maltose hydrate.	Maltose, anhydrous.
50	30·6	29·1	180	107·7	102·3
55	33·6	31·9	185	110·8	105·3
60	36·5	34·7	190	114·0	108·3
65	39·4	37·5	195	117·1	111·3
70	41·4	39·3	200	120·3	114·3
75	45·3	43·1	205	123·5	117·3
80	48·3	45·9	210	126·7	120·3
85	51·2	48·6	215	129·9	123·3
90	54·1	51·4	220	133·1	126·4
95	57·0	54·2	225	136·4	129·6
100	59·9	57·0	230	139·8	132·8
105	62·9	59·8	235	143·2	136·0
110	65·8	62·6	240	146·7	139·3
115	68·8	65·4	245	150·2	142·6
120	71·7	68·2	250	153·7	146·0
125	74·6	71·0	255	157·3	149·4
130	77·6	73·8	260	161·0	152·9
135	80·6	76·6	265	164·8	156·6
140	83·6	79·4	270	168·7	160·3
145	86·5	82·2	275	172·7	164·1
150	89·5	85·0	280	176·7	167·9
155	92·5	87·9	285	180·7	171·7
160	95·5	90·7	290	184·9	175·7
165	98·5	93·6	295	189·5	180·0
170	101·5	95·5	298·6	195·0	185·2
175	104·6	99·4			

The factor, Cu/maltose, employed in calculating the above table varies somewhat: it is 1·636 for 25 milligrams of maltose hydrate, 1·676 for 75 milligrams, and 1·531 for 195 milligrams.

J. B. T.

Estimation of Milk-sugar. By J. Knowles and J. A. Wilson (*Chem. News.*, **63**, 191—192).—The authors have compared the estimation of milk-sugar in milk by optical methods with determinations made gravimetrically and volumetrically:—1. By Fehling's solution: Removing caseïn with acetic acid, precipitating in a neutral solution, and weighing as cupric oxide. 2. By running the diluted milk into boiling Pavy-Fehling solution. 3. By treating the milk, after the removal of caseïn by acetic acid, as in method 2. One set of results obtained was as follows :—

Method.	1.	2.	3.	Optical A.	Optical B.
Anhydrous sugar per cent.	4·63	4·71	4·78	5·03	4·92

In optical method A, 70 c.c. of milk is treated with 5 c.c. of basic lead acetate, agitated, diluted to 100 c.c., and the observation taken at 60° in a 200 mm. tube. In method B, 50 c.c. of milk is treated with $2\frac{1}{2}$ c.c. of basic lead acetate and 1 c.c. of mercuric nitrate, agitated, diluted to 57 c.c., and the observation taken in a 220 mm. tube. In both cases, an instrument of the Laurent type was used, and the specific rotation of lactose for the D line was taken as 52·5. The Pavy-Fehling method is regarded as rapid and accurate, but the optical is preferred. When cane-sugar is present in the milk, the amount can be ascertained from the data obtained by noting both the optical activity and the reducing power. D. A. L.

Asbestos Method of Milk Analysis. By F. T. Shutt (*Chem. News*, **63**, 160—161).—Numerous comparative experiments made with the asbestos and other methods of examining milk have led the author to declare in favour of the former method. Milk is weighed into tubes containing asbestos fibre, previously dried in a steam cupboard, then placed in a steam cupboard, through which a strong current of air passes, for 12 or 16 hours, at a temperature between 85° and 90°, and subsequently cooled in a desiccator and weighed. The numbers obtained are 0·34 to 0·49 per cent. lower than those obtained in the ordinary platinum dish method; there is, moreover, no browning of the residue apparent in the asbestos treatment: reasons for these differences are suggested. Fat determinations by various methods did not differ much, but in some experiments slightly higher results were obtained by extracting in Soxhlet tubes and weighing the fat directly than in exhausting the solids in asbestos by means of Stutzer tubes, the increase being attributable to oxidation of the fat, inasmuch as in comparative exhaustions with Soxhlet and Stutzer tubes the latter not only yielded the higher results, but also proved more rapid. Numerous results of analyses are quoted to show that the asbestos method yields concordant numbers. D. A. L.

Apparatus for the Estimation of the Fat in Milk. By E. Molinari (*Ber.*, **24**, 2204—2209).—Of the numerous methods which have been proposed for estimating the fat in milk, the simplest and the quickest is that of Stokes (Abstr., 1890, 304); although many chemists have testified to the accuracy of Stockes' method, it is nevertheless attended with several sources of error. The author describes a form of apparatus with which, it is claimed, the fat determination in a sample of milk can be accurately carried out by Stokes' process in 30—35 minutes.

This apparatus consists of a flask A, about 90 c.c. in capacity, which is provided with a removable glass cover, and a second flask B, about 75 c.c. in capacity, to the neck of which is fused a glass cock pierced in three directions. The ground neck of the flask B can be fitted air-tight into that of A so that the whole apparatus is shaped something like a sand glass; one of the apertures in the glass cock on the flask B is connected with a capillary tube passing to the bottom of the flask B, and one with a capillary tube passing to the bottom of the flask A, whilst the third aperture serves to open communication between the air outside and the interior of either of the two flasks; the flask A and its cover are tared once for all.

The analysis is carried out as follows:—The milk (10 c.c.) and concentrated hydrochloric acid (10 c.c.) are placed in the flask A, the mixture carefully heated to boiling, and the boiling continued for not longer than 1½ minutes, the mixture being shaken from time to time; after cooling in water, alcohol-free ether (25 c.c.) is added, the flask B is fitted on to the flask A with the cock closed, and the whole is shaken for a few minutes, the pressure inside and outside being equalised occasionally in the usual manner. The whole apparatus is then inverted and, after 5—6 minutes, the dark-brown acid liquid is drawn off into the flask B, and the cock is closed; the apparatus is now inverted again, the flask A containing the ethereal solution is disconnected, a fresh quantity of ether (10 c.c.) is introduced into the flask B, and the mixture well shaken. The acid liquid is finally drawn off, the ethereal solution in the flask B mixed with that in the flask A, the whole washed two or three times with a little water, the water being drawn off with the aid of the flask B, and the ether evaporated. The fat remaining in the flask A is finally heated at 107—110° for at least 10 minutes and twice shaken vigorously to aid the escape of water; after cooling in a desiccator, the flask is weighed until constant. The results agree very well with those obtained by Soxhlet's process, the greatest difference being +0·08 per cent. when the milk is weighed and 0·04 per cent. when the milk is measured.

The apparatus can also be employed in a large number of other qualitative and quantitative analytical processes. F. S. K.

Estimation of Water in Butter. By O. HENZOLD (*Bied. Centr.*, **20**, 429; from *Milchzeit.*, **20**, 71—72).—20 grams of ignited and cooled (in desiccator) pumice is weighed in a flat dish with a glass rod, into which the butter (10—2 grams) is put. The butter is melted in a drying oven, stirred, and dried for two hours in a water oven. More prolonged drying is not advisable as the butter will increase in weight. The results of several analyses are given in the original paper, showing the method to be trustworthy. N. H. M.

Detection of Margarin in Butter. By R. LÉZÉ (*Compt. rend.*, **112**, 813—815).—The attraction of strong syrup for the water contained in butters is utilised to produce practically the same effect as centrifugal separation. 1·5 c.c. of concentrated syrup is placed in a tube provided with a stopper, and having a mark indicating a volume of 10 c.c. The tube is heated in warm water, and butter is added gradually until the total volume of the contents of the tube is 10 c.c.

The tube is then agitated, tightly stoppered, attached to a strong piece of twine, and swung round rapidly for a short time.

Pure butter separates into an upper layer of transparent fat, an intermediate layer of milky emulsion, and a lower layer of syrup. Margarin, on the other hand, shows no clear layer of fat, and the whole remains as an emulsion, with the exception of the lower layer of syrup. This difference makes it possible to detect 15 per cent. of margarin.

Further, butter containing margarin shows, to a greater or less extent, that tendency to remain in superfusion which characterises the fat of margarin, and if tubes of genuine and suspected butter are allowed to cool together, the rate of solidification affords a valuable indication as to purity. C. H. B.

Examination of Butter and Fats. By J. König and F. Hari (*Zeit. anal. Chem.*, **30**, 292—300).—The amount of the volatile fatty acids in butter, as found by Reichert's process, is not sufficiently constant to allow of the indirect estimation of butter-fat in margarin with any approach to accuracy. The amount of the soluble barium salts obtainable by saponifying the butter fat by barium hydroxide is far less variable, and at the same time exceeds enormously the proportion yielded by most of the other fats whose presence is at all likely. The process employed is as follows:—5 grams of the fat is dissolved in 60 c.c. of hot alcohol, 40 c.c. of hot baryta water (17·5 grams of barium hydroxide per 100 c.c.) is added, and the whole boiled for 3—3½ hours with reflux condenser. When cold, water is added to 300 c.c., and after mixing and filtering, 250 c.c. is treated with carbonic anhydride until the alkaline reaction has disappeared. It is then evaporated to dryness, redissolved, made up to 250 c.c., and filtered. The barium in 200 c.c. of the filtrate is determined as sulphate, and the amount of barium oxide corresponding with 5 grams of the fat is called its "Baryta number." The following values were found for a variety of fats.

Fat.	Baryta number.	Fat.	Baryta number.
	milligrams.		milligrams.
Linseed oil	18·7	Butter *a*	238·5
Poppy oil	7·0	,, *b*	216·9
Olive oil	9·4	,, *c*	221·5
Rape-seed oil	17·6	,, *d*	216·4
Sesame oil	6·9	,, *e*	236·0
Earth-nut oil	22·9	,, *f*	199·6
Cotton-seed oil	29·1	Beef tallow	35·8
Fish oils	25·2 to 52·8	Mutton tallow	4·9
Palm-kernel oil	86·3	Lard	17·08
Cocoa-nut oil	118·46	Margarin *a*	21·6
Cocoa butter	195·1	,, *b*	21·7
		,, *c*	22·8

M. J. S.

Estimation of Turpentine in Paints and Varnishes. By H. J. Phillips (*Chem. News*, **63**, 275).—Distillation in a current of coal gas is found to be efficient. A ⊢-piece is fitted into the tubulure of a retort, the side tube being connected with the gas supply, whilst the other serves for the thermometer; a tube from the end of the retort passes through one hole in the stopper of a cooled tared receiver, whilst the other hole in the stopper carries a short piece of tubing, from which the coal gas escapes and is ignited; during the distillation, the supply is regulated to sustain a very small flame. In this way the whole of the turpentine is obtained, and, moreover, the residuary products are in a fit condition to be further examined.

D. A. L.

Examination of Chinese Tea. By P. Dvorkovitch (*Ber.*, **24**, 1945—1955).—The author criticises the methods of Peligot, Mulder, and Zöller for the estimation of theïne in tea, and, regarding them as unsatisfactory, has devised the following process, which is said to be both rapid and exact. Ten grams of the finely powdered tea is treated with three successive quantities of 200 c.c. of boiling water, five minutes being allowed for each digestion, and then boiled with two successive quantities of 200 c.c. of water, or more, if necessary, until the last extract is almost, if not quite, free from colour. The extracts are made up to a litre, and extracted thrice with light petroleum to remove oil, &c.; 600 c.c. of the washed solution is then shaken with 100 c.c. of baryta water containing 4 grams of baryta in solution, filtered, and 583 c.c. of the filtrate (corresponding with 5 grams of tea) mixed with 100 c.c. of salt solution (20 grams of salt in 100 c.c. of water), and thrice extracted with chloroform. The extraction is best effected by shaking successive small quantities of the solution with chloroform, since nothing further can be extracted from the solution after the third shaking under these conditions, and not more than 400 grams of chloroform is required. After removal of the chloroform, by distillation to a small bulk and subsequent evaporation in a small dish and drying at 100°, the theïne is obtained in perfectly white needles.

In the preparation of black tea the leaves are submitted to a fermentation, which has a most important influence on the quality of the product, and, as Geissler has shown, is carried on at the expense of the tannin. With the object of estimating not only the tannin but also the decomposition products formed from it during the fermentation, or, in other words, determining the extent of the fermentation, the author has improved Lowenthal's method of oxidation with potassium permanganate in the presence of indigo-carmine. The solutions required are the following:—(1.) Decinormal oxalic acid; (2) a potassium permanganate solution of such a strength (approximately 2·6 grams in the litre) that 130 grams are equivalent to 100 grams of decinormal oxalic acid; (3) dilute sulphuric acid containing 200 grams of ordinary acid to a litre of water; (4) baryta-water containing 4 grams of baryta to 100 c.c. of water; and (5) an indigo-carmine solution prepared by mixing 50 grams of pure indigo-carmine paste with water, adding 50 grams of sulphuric acid and a litre of water, filtering, and diluting until 25 c.c. of the solution

Water.	Theïne.	Tannin.	Fermentation products.	Extractive matter.	Total amount of theïne, tannin, and fermentation products.	Relative proportions.		
						Theïne.	Tannin.	Fermentation products.
						per cent.	per cent.	per cent.
7·44	2·14	9·44	1·80	33·43	13·38	16·00	70·55	13·45
7·79	2·50	9·87	1·81	33·33	13·98	17·89	70·60	11·51
8·29	2·53	9·27	1·68	32·11	13·48	18·78	68·76	12·46
—	2·68	10·05	1·44	37·26	14·17	18·92	70·92	10·16
7·97	2·66	9·77	1·55	34·55	13·98	19·03	69·89	11·08
8·16	2·65	9·76	1·45	31·20	13·86	19·13	70·41	10·46
7·66	2·72	9·59	1·78	30·70	14·09	19·31	68·06	12·63
—	2·91	10·38	1·52	33·88	14·81	19·65	70·09	10·26
7·60	3·00	10·55	1·67	34·00	15·22	19·79	69·31	10·90
—	2·87	10·05	1·74	33·90	14·66	19·82	68·50	11·68
—	2·83	10·07	1·35	33·15	14·25	19·87	70·66	9·47
8·07	2·88	9·65	1·65	30·92	14·17	20·33	68·10	11·57
—	2·82	9·36	1·59	33·00	13·77	20·55	67·90	11·55
—	3·11	10·03	1·70	32·21	14·84	20·96	67·59	11·45
8·10	3·00	9·36	1·88	34·12	14·24	21·02	65·73	13·25
—	3·10	10·00	1·50	34·10	14·60	21·23	68·50	10·27
—	3·16	9·80	1·75	33·66	14·71	21·48	66·62	11·90
—	3·02	9·37	1·50	32·40	13·89	21·74	67·46	10·80
9·08	3·00	9·45	1·18	33·80	13·63	22·02	69·33	8·65
7·84	3·00	8·84	1·18	32·20	13·02	23·05	67·89	9·06
8·85	3·02	9·05	0·90	33·00	12·97	23·29	69·77	6·94
8·20	3·27	9·21	1·44	34·95	13·92	23·50	66·18	10·34
8·24	3·25	9·14	1·25	32·93	13·64	23·84	67·00	9·16
9·13	3·41	9·32	1·44	33·26	14·17	24·07	65·77	10·16
9·78	3·33	9·22	1·27	32·00	13·82	24·11	66·71	9·18
8·42	3·45	9·42	1·38	34·80	14·25	24·22	66·10	9·68
7·83	3·21	9·00	1·17	33·46	13·38	24·52	67·26	8·22

require 20 c.c. of the permanganate for oxidation. The tea solution (10 grams in the litre) is prepared as already described, and of this 40 c.c. is diluted with 500 c.c. of water, treated with 25 c.c. of the indigo-carmine solution and 25 c.c. of dilute sulphuric acid, and titrated with permanganate until the yellow colour becomes evident. The manner in which the permanganate is added is of considerable importance, and the author states that in the titration of the indigo-carmine solution 18 c.c. of the permanganate is added at the rate of 2—3 drops per second, and the remainder at the rate of 1 drop per second, and that in the titration of the tea with indigo-carmine 23 c.c. of the permanganate is run in first of all, then 2—3 drops per second is added, and finally only 1 drop per second until the reaction is completed. If more than 38 c.c. of permanganate is required in the latter titration, a smaller quantity of the tea solution should be taken for the analysis. The amount of the fermentation product is then estimated. For this purpose, 80 c.c. of the tea solution is mixed with 20 c.c. of baryta-water, filtered, and 50 c.c. of the filtrate corresponding with 1/25th of the tea extract is diluted with 500 c.c. water, mixed with 25 c.c. of dilute sulphuric acid, then with 25 c.c. of the indigo-carmine solution, and titrated with permanganate, 18 c.c. of the solution being run in, first of all, then 2—3 drops per second added, and finally 1 drop a second until the reaction is ended. The amount of permanganate employed, less that required for the oxidation of the indigo-carmine, indicates the amount of decomposition products of tannin, or, more correctly, the degree of fermentation which the tea-leaves have undergone. The percentage of tannin and of the fermentation product is calculated by multiplying the weight of oxalic acid equivalent to the number of c.c. of permanganate employed in the oxidation by 31·3, since 63 grams of oxalic acid, according to the author's experiments, correspond with 31·3 grams of tannin, and not with 41·2 grams as stated by Neubauer.

With regard to the comparative values of teas, the author states that the higher the proportion of theïne to the total amount of tannin and fermentation products, the more valuable is the tea. The analyses (p. 1303) of teas of the first crop of 1890 are quoted in the paper.

W. P. W.

Quantitative Estimation of Proteïds. By L. Devoto (*Zeit. physiol. Chem.*, **15**, 465—476).—As all proteïds but peptones (and deuteralbumose derived from protalbumose) are precipitated by heat and ammonium sulphate, a method is suggested by means of which the most ordinarily occurring proteïds in effusions, blood, urine, &c., may be estimated. In a few cases, however (four cases of pneumonia and one of phthisis with empyema), true peptonuria was observed to occur.

The method consists in precipitating the proteïds by saturating with ammonium sulphate and boiling; the reaction of the liquid may be acid, neutral, or alkaline. The precipitate is collected, washed, and weighed in the usual manner.

W. D. H.

General and Physical Chemistry.

New Bands and Lines in the Emission Spectrum of the Ammonia-Oxygen Flame. By J. M. Eder (*Monatsh.*, **12**, 86—88; compare Magnanini, Abstr., 1890, 97).—By employing the method of spectrophotographic investigation, the author has discovered in the spectrum of the ammonia-oxygen flame some 240 new lines having wave-lengths varying from $\lambda = 5000$ to $\lambda = 2262$ in the extreme ultra-violet.

The emission spectrum of ammonia shows seven very characteristic bands, one of which occurs between the red and the ultra-violet, and the other six, five of which much resemble each other, in the ultra-violet. The wave-lengths corresponding with the most important lines in the different bands have been determined, and are given in this preliminary communication. G. T. M.

Molecular Refractive Energy of some Triethylsulphine Derivatives. By R. Nasini and T. Costa (*Gazzetta*, **21**, 217—228).—From a determination of the molecular refractive energy of triethylsulphine iodide (*Gazzetta*, **21**, 188), the authors recently calculated an exceptionally high value for the molecular refractive energy of the sulphur in these compounds. The following experiments were accordingly made with the iodide, chloride, and hydroxide of triethylsulphine, in order to determine the extent of this variation and the effect of the presence of oxygen in the molecule. The principal results obtained are exhibited in the table on p. 1306, from which it appears that the molecular refractive energy of the iodide remains constant in the same solvent, but varies in different solvents; the value calculated for the sulphur is accordingly very high. The chloride yields similar, but slightly lower, values.

Walter's constants (Abstr., 1890, 202) were also calculated with moderately concordant results. The introduction of oxygen into the molecule occasions a considerable fall in the molecular refractive energy of sulphur, although the type of the compound remains unchanged. The decreasing values given by sulphur in compounds built up on the types of R'_2SO, SO_2, and SO_3 (*Rend. R. Acad. Lincei*, 1885, 1) indicates the existence of some relation which is at present being further investigated. S. B. A. A.

Strength of Solutions Estimated by their Refraction. By H. O. G. Ellinger (*J. pr. Chem.* [2], **44**, 152—157).—The author uses an Amagat-Jean oleo-refractometer, but prefers to call it a "difference-refractometer." The rays from a stearin candle are passed first through a collimator which has a vertical shutter in place of a slit, movable by a millimetre screw, and then through the solution to be tested, contained in a hollow glass prism which is surrounded by a glass cell with parallel sides, itself surrounded by a similar cell

	SEt_3I.									SEt_3Cl.	$SEt_3{\cdot}OH$.		
Solvent.	Water.				Alcohol.			Acetic acid.		Water.	Water.		
Concentration .	3·5413	9·6751	11·4625	27·3240	4·7004	6·2329	6·8372	3·6090	3·9721	3·6130	2·5157	3·4001	7·4063
Temperature ..	10·3	10·7	9·4	12·3	20	20	28·8	21·2	21·1	11·6	21	21·6	21·4
Density of the solution	1·01173	1·03366	1·03925	1·10516	0·81133	0·8789	0·81277	1·06389	1·06604	1·00274	1·00115	1·00175	1·00626
$m_{H\alpha}$	1·33722	1·34739	1·35011	1·37979	1·36702	1·36906	1·36571	1·37626	1·37713	1·33859	1·33647	1·33818	1·34667
$P\frac{m_{H\alpha}-1}{d}$	93·05	92·82	92·81	92·30	96·16	95·62	95·08	95·27	95·15	76·66	68·96	68·82	68·71
Mol. ref. energy of sulphur ..	18·65	18·42	18·41	17·90	21·76	21·22	20·68	20·87	20·75	17·26	15·66	15·52	15·41
$P\frac{m_{H\alpha}^2-1}{(m_{H\alpha}^2+2)d}$ ..	55·01	54·96	54·96	54·46	59·38	58·25	57·34	55·13	55·00	45·57	40·85	40·81	40·73
Mol. ref. energy of sulphur ..	10·56	10·49	10·49	9·99	14·91	13·78	12·87	10·66	10·53	9·07	7·75	7·71	7·63

into which warm water can be placed to raise the temperature. The field of the telescope, which is fixed on the same axis as the collimator, contains a glass scale graduated into 100 parts, 40 on the left, and 60 on the right of the zero. This scale can be moved to the right or left by a fine adjustment. It will be seen that the field is thus divided into light and dark.

The cells are first filled with distilled water and the scale moved until the edge of the dark space corresponds with the zero mark; the solution to be tested is then put into the prism in place of the water, distilled water remaining in the other cells. The solution, having a greater refractive index than the water, will cause the boundary line of the dark space to move to the right or left, according to the position of the prism, to a greater or less extent in proportion to its strength. For instance, a solution of sodium chloride containing 0·01 per cent. shifts the dark space 0·75 division; a solution containing 1 per cent. shifts it 7·5; one containing 2 per cent. shifts it 15. The greatest accuracy is attained by diluting a solution which gives a high deflection.

The author, by using solutions of known strengths, has calculated the "parts per thousand factor" for various salts, that is, the number by which the deflection must be multiplied in order to find the parts of the solid per thousand of the solution. A table of these factors, together with examples of the accuracy attainable, is given. The method is applicable to salts, sugar, dextrin, gum, and alcohol, and is exceedingly rapid. A. G. B.

Electrical Conductivity of Solid Electrolytes. By J. ROSENTHAL (*Ann. Phys. Chem.* [2], **43**, 700—722).—The author has investigated the influence of temperature on the conductivity of electrolytes, using Kohlrausch's method, and making contact with mercury, or (above 100°) with Rose's fusible alloy. He finds that exact quantitative determinations can scarcely be made, on account of the uncertainty involved in imperfect electrical contact of the electrolyte with the metallic part of the circuit, so that his numbers have only a relative value. The conductivity of the substances studied increases as the temperature is raised. Solid lead chromate kept at a constant high temperature exhibits a diminishing conductivity with the time, the rate of diminution being the greater as the temperature is higher.

Lead chloride, bromide, and oxide conduct better at any definite temperature if they have been previously exposed to a higher temperature. Lead chloride, bromide, and iodide are all very plastic below their melting points—a fact which explains, in the author's opinion, why the melting point is not a singular point in the curve of conductivity, as Graetz observed in numerous instances.

The conductivity was found to depend to a great extent also on the state of aggregation of the solid: for example, lead chloride which had been precipitated and compressed had a much greater resistance than the same substance when fused, powdered, and then compressed. J. W.

Molecular Changes in Metals as shown by their Electrical Conductivity. By H. Le Chatelier (*Zeit. physikal. Chem.*, **8**, 183—187).—That molecular changes take place abruptly at certain temperatures in certain metals which are being heated has already been shown by Osmond (Abstr., 1887, 14 and 219), these molecular changes being indicated by sudden changes in the physical properties of the metals at the point in question. The author endeavoured to measure the changes in length which accompany these molecular changes, but owing to experimental difficulties could obtain no satisfactory results, except in the case of steel, a sample of which containing 0·9 per cent. of carbon showed a sudden increase in length of 1 mm. per metre at the point of recalescence (730°). Measurements of the electrical conductivity, on the other hand, led to more definite results. Metals which undergo no molecular changes have a conductivity which increases uniformly with the temperature. The same law holds also for the other metals above the temperature at which the last change takes place, for instance, for nickel above 340°, and for iron above 850°. Below these points, the increase in conductivity with the temperature is not uniform, but the temperature coefficient undergoes abrupt changes at certain places.

The point of change of iron, 850°, is not changed by the presence of either large or small quantities of carbon and silicon. Alloys of iron and nickel do not show two points of change each corresponding with that of the metals alone, but have only one point of change, which occurs somewhere between that of nickel, 340°, and that of iron, 850°. This behaviour leads to the conclusion that in these alloys the iron and nickel are not merely mechanically mixed, but have entered into more intimate combination, either in the form of a chemical compound or an isomorphous mixture. Alloys of nickel with copper and zinc behave, on the other hand, as mixtures of these metals, the change not taking place abruptly at any particular temperature, but being distributed over an interval of about 100°. Ferronickel containing 25 per cent. of nickel and 0·8 per cent. of carbon shows in its normal state no point of molecular change above 0°, but when treated with moist hydrogen, which oxidises the carbon, it becomes magnetic, and on heating has a point of change at 550°. On cooling, however, the reverse change only takes place at somewhere between 0° and 100°.

In the course of these experiments, the author had occasion to observe that silver above 600° absorbs hydrogen, this absorption causing a lowering of 30° in the melting point of the metal.

H. C.

Molecular Conductivity of Acids in various Solvents. By K. Hartwig (*Ann. Phys. Chem.*, **43**, 839—840).—The author gives the molecular conductivity and temperature coefficient [α in the formula $k_t = k_0\,(1 + \alpha t + \beta t^2)$] of formic, acetic, butyric, and oxalic acids dissolved in methyl, ethyl, and amyl alcohols. As in the case of aqueous solutions, the molecular conductivity usually increases with increasing dilution; but there are exceptions to this rule. For example, formic acid in ethyl and in methyl alcohol, and oxalic acid in ethyl alcohol, show maxima and minima in the curve for molecular conductivity. When the molecular conductivity is at a maximum, the temperature coefficient is at a minimum, and *vice versâ*.

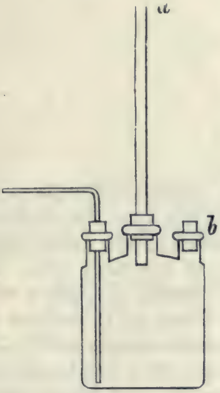
J. W.

Electrochemical Investigations. By F. EXNER (*Monatsh.*, **12**, 276—303).—The author has measured the difference in potential between various metals on the one hand and aqueous solutions of the halogens and halogen acids of different concentration on the other; the method employed is identical in principle with that previously described (Abstr., 1889, 456), and the results are given in tables, and in the form of curves. F. S. K.

Formulæ for Electrolytic Dissociation. By J. D. VAN DER WAALS (*Zeit. physikal. Chem.*, **8**, 215—222).—Considering the formulæ for electrolytic dissociation, the author arrives at conclusions similar to those of Arrhenius, that the heat generated by the union of the ions of a salt is either very small or, in some cases, even negative. This result may be explained by assuming that the attraction between the ions and the solvent is very great, greater in some cases, even, than that between the ions themselves. H. C.

The Nature of Flame. By N. TECLU (*J. pr. Chem.* [2], **44**, 246—255).—The author describes the following experiment made with Heumann's "Gas Explosion Apparatus," Fig. 1. When the Woulffe's bottle is filled with illuminating gas by the bent tube, and the latter lighted at *a*, on shutting off the gas and removing the stopper at *b*, air enters, and the flame gradually loses its luminosity, going through a succession of changes; finally, a greenish-coloured cone is formed inside the flame, which diminishes rapidly in size, divides from the outer portion, and passes down the tube as a separate flame until it reaches the bottle, when the mixture of air and gas in it explodes.

FIG. 1.



A modification (Fig. 2) of the apparatus was then devised. A has a capacity of 1 litre, and is furnished with a tube B, 350 mm. long and 10 mm. in diameter, the tube C serving to pass in the gas. On lighting the gas at *f* and shutting off the supply, the same phenomena are observed as with Heumann's apparatus, and, if air is passed through C at the moment when the flame divides, the separated portion of the latter passes downwards with increased rapidity; when, however, the tube C is pushed up, so that *a* is as near as possible to *g*, and gas is passed through it, the flame is again driven upwards; whence it appears that the downward motion of the flame is dependent on the velocity of the combustion, and, since the motion of the gaseous mixture is upward, and, therefore, in the opposite direction to that of the flame, the latter will take up a position corresponding with the resultant of these two motions.

FIG. 2.

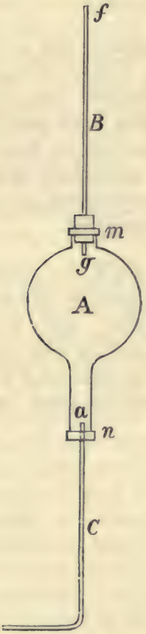
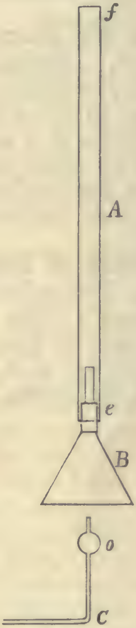


FIG. 3.



By employing the apparatus shown in Fig. 3, the author has succeeded in bringing the lower flame to a fixed position. A is a tube 600 mm. long and 20 mm. in diameter, and has a funnel, 80 mm. in diameter, attached to it by means of a stopper; C is a tube 3 mm. in diameter, having a bulb *o* sufficiently large to close the funnel when placed in the apex. If *o* is inserted into the funnel, a stream of gas passed up, and, after lighting it at *f*, the tube C be lowered, air will enter with the gas, the flame loses its luminosity, and soon becomes bluish, and, on further lowering C, the flame (as in the experiment first described) divides. When the gas pressure is constant and the air quite still, the flame which has descended into the tube A can be kept in the same position for any length of time. It is then seen that the cooler upper flame at *f*, which obtains its oxygen from the surrounding air, has its surface turned upwards, whilst that of the lower greenish-coloured and very hot flame is turned downwards. A portion of the gas is therefore burnt in the tube by means of the air mixed with it; whilst the other portion passes upwards and is burnt in the upper flame. By raising C both flames can be made to approach one another, and, when in contact, a flame resembling that of a Bunsen burner results. The Bunsen burner flame, therefore, appears to consist of two conical flames of different heights: in the outer one that part of the gas which escapes burning in the inner flame is burnt at a relatively low temperature by the outside air, whilst in the inner flame, the height of which is conditioned by the velocity of the combustion (see above), the gas is burnt by the air entering from below. When the amount of gas passing into a Bunsen burner is diminished so that the relative quantity of air is increased to such an extent that the flame divides, it burns below. The structure of the Bunsen flame can be shown by holding within it strips of wood 200 mm. long, 100 mm. wide, and 5 mm. thick, charred figures being produced; the burners which give the best indications are those in which the difference in the height of the two flames is large. These figures represent horizontal or longitudinal sections of the flame according to the position in which the strips of wood are held, and they show that in the inner flame the heating surface inclines towards the centre, whilst in the outer flame it inclines outwards. A. R. L.

Thermochemistry of Organic Chlorine Compounds. By BERTHELOT and MATIGNON (*Compt. rend.*, **112**, 1102—1107).—Determinations of the heat of formation and heat of combustion of carbon compounds containing chlorine have hitherto been inaccurate in consequence of the difficulty of converting the chlorine into a definite product. Accurate results can, however, be obtained by exploding the compound in the calorimetric bomb in presence of a solution of arsenious acid. All the chlorine is thus converted into hydrochloric acid, and the arsenious acid remaining is estimated. Carbon chlorides and other compounds rich in the halogen are mixed with camphor before being burned. The following results were obtained :—

	Heat of combustion. Constant volume.	Heat of combustion. Constant pressure.	Heat of formation.
Orthodichlorobenzene (solid)....	676·4 Cal.	676·7 Cal.	+36·7 Cal.
Hexachlorobenzene (solid)......	532·4 ,,	531·6 ,,	+63·0 ,,
Hexachlorethane (solid)........	132·0 ,,	131·2 ,,	+86·2 ,,
Tetrachlorethylene (liquid)	182·3 ,,	181·8 ,,	+26·0 ,,
Carbon tetrachloride (liquid)....	59·3 ,,	58·8 ,,	+54·2 ,,
Chloroform (liquid)	100·15 ,,	99·95 ,,	+43·2 ,,

C_6H_6 gas + $6Cl_2$ = C_6Cl_6 sol. + 6HCl gas	develops	+205·2 Cal.
C_2H_6 + $6Cl_2$ = C_2Cl_6 sol. + 6HCl gas	,,	+193·0 ,,
C_2H_4 + $4Cl_2$ = C_2Cl_4 liq. + 4HCl gas	,,	+128·8 ,,
C_2Cl_4 liq. + Cl_2 = C_2Cl_6 sol.	,,	+60·0 ,,
CH_4 + $4Cl_2$ = CCl_4 gas + 4HCl gas	,,	+116·5 ,,
CH_4 gas + $3Cl_2$ = $CHCl_3$ gas + 3HCl gas	,,	+83·1 ,,

The substitution of chlorine in the gaseous state develops 30 to 32 Cal. per atom in the paraffin series, and a slightly greater quantity of heat in the benzene series. The addition of chlorine causes almost exactly the same thermal disturbance. C. H. B.

Constitution and Heat of Formation of Bibasic Erythroxides. By De Forcrand (*Compt. rend.*, **112**, 1133—1136) :—

$C_4H_8Na_2O_4$:—Heat of dissolution at 15° +12·49 Cal.; heat of formation (C and Na sol., H and O gas) +307·8 Cal.
$C_4H_8Na_2O_4,4H_2O$:—Heat of dissolution at 15° −2·25 Cal.
$C_4H_8Na_2O_4,2NaOH$:—Heat of dissolution +29·28 Cal.
$C_4H_8Na_2O_4,2NaOH,9\frac{1}{2}H_2O$:—Heat of dissolution +1·79 Cal.

From these results it follows that—

$C_4H_9NaO_4$ sol. + NaOH sol. = $C_4H_8Na_2O_4$ sol. + H_2O sol.	develops	−0·725 Cal.
$C_4H_8Na_2O_4$ sol. + H_2O liq. = $C_4H_9NaO_4$ sol. + NaOH sol.	,,	+2·155 ,,
$C_4H_6NaO_4$ sol. + $\frac{1}{2}Na_2O$ sol. = $C_4H_8Na_2O_4$ sol. + $\frac{1}{2}H_2O$ sol.	,,	+16·28 ,,
$C_4H_9NaO_4$ sol. + Na sol. = $C_4H_8Na_2O_4$ sol. + H gas	,,	+31·165 ,,
$C_4H_{10}O_4$ sol. + Na_2 sol. = $C_4H_8Na_2O_4$ sol. + H_2 gas	,,	+69·305 ,,

$C_4H_8Na_2O_4$ sol. + $4H_2O$ sol. = $C_4H_8Na_2O_4,4H_2O$ sol.	,,	+9·02 ,,
$C_4H_8Na_2O_4$ sol. + $4H_2O$ liq. = $C_4H_8Na_2O_4,4H_2O$ sol.	,,	+14·74 ,,
$C_4H_8Na_2O_4$ sol. + 2NaOH sol. = $C_4H_8Na_2O_4,2NaOH$ sol.	,,	+2·93 ,,
$C_4H_8Na_2O_4,2NaOH$ sol. + $9\frac{1}{2}H_2O$ sol. = $C_4H_8Na_2O_4,2NaOH,9\frac{1}{2}H_2O$ sol.	,,	+13·91 ,,
$C_4H_8Na_2O_4,2NaOH$ sol. + $9\frac{1}{2}H_2O$ liq. = $C_4H_8Na_2O_4,2NaOH,9\frac{1}{2}H_2O$ sol.	,,	+27·49 ,,

The addition of sodium hydroxide to disodium erythroxide develops heat, and hence a true compound is formed. The heat of hydration of the erythroxides is practically constant for the same proportion of water, but is always small; hence the alteration of the hydrates in solution. The thermal disturbances indicate that the compounds have the constitution indicated by the formulæ given. In all the reactions, the thermal disturbances are about +7 Cal. lower than they would be if $C_4H_{10}O_4$ were substituted for $C_4H_9NaO_4$, and hence the two primary hydroxyl groups have not the same function. C. H. B.

Thermochemistry of Propionic Acid and of the Alkaline Propionates. By G. MASSOL (*Compt. rend.*, **112**, 1136—1137.—*Propionic Acid.*—Heat of dissolution +0·62 Cal.; heat of neutralisation by potassium hydroxide in solution +12·95 Cal., by sodium hydroxide +12·49 Cal., these values being practically identical with the corresponding values for acetic and butyric acids.

Potassium propionate forms a white, crystalline mass, which becomes anhydrous at 100°; heat of dissolution +3·02Cal; $C_3H_2O_2$ liq. + KOH sol. = $C_3H_5KO_2$ sol. + H_2O sol. develops +24·44 Cal., a number identical with the corresponding number for potassium acetate.

Sodium propionate crystallises with 2 mols. H_2O, becomes anhydrous at 100°, and is very deliquescent; heat of dissolution of the anhydrous salt +3·05 Cal.; $C_3H_6O_2$ liq. + NaOH sol. = $C_3H_5NaO_2$ sol. + H_2O sol. develops +21·27 Cal., the corresponding number for sodium acetate being +27 Cal., and for sodium butyrate +21·7 Cal.
C. H. B.

Heat of Dissolution of Carbon Compounds in various Alcohols. By W. TIMOFÉEFF (*Compt. rend.*, **112**, 1137—1139 and 1223—1225). The solubility is expressed (table, p. 1314) in terms of the number of molecules of alcohol required to dissolve 1 mol. of the acid. The heats of dissolution were measured at 12—14°.

In the case of the two bibasic acids, the molecular solubility decreases as the molecular weight of the alcohol increases, whilst the heat of dissolution varies in the contrary direction. In the case of the monobasic acids, the values are all somewhat close, but an increase in the heat of dissolution is accompanied by a decrease in the molecular solubility.

Experiments with the same three alcohols and cadmium iodide, mercuric chloride, naphthalene, and carbamide show that the same law holds good, namely, increased heat of dissolution corresponds with a lower molecular solubility. In the case of methyl alcohol and mercuric chloride, the curve of solubility indicates the formation of a compound. A solution $HgCl_2 + 25CH_4O$ deposits at 0° crystals of the composition $HgCl_2,2CH_4O$, but at 35°, this solution behaves like the others. Carbamide is an exception; the solubility and heat of dissolution in ethyl alcohol are both greater than the corresponding numbers for propyl alcohol.

The ratio of the heat of dissolution of one and the same substance in methyl alcohol to its heat of dissolution in ethyl alcohol is practically identical with the ratio of its heat of dissolution in ethyl alcohol to its heat of dissolution in propyl alcohol. C. H. B.

Thermochemistry of the Camphene Series. By BERTHELOT and MATIGNON (*Compt. rend.*, **112**, 1161—1170).—The combustions

	Methyl alcohol.		Ethyl alcohol.		Propyl alcohol.	
	Heat of diss.	Solubility.	Heat of diss.	Solubility.	Heat of diss.	Solubility.
Oxalic acid (anhydrous)	−0·87	—	−1·27	—	−1·88	—
Oxalic acid (hydrated)	−5·21	7·75 at −1°	−5·56	9·65 at −1°	−6·60	15·4 at −1°
,, ,,	—	5·95 at 20°	—	7·45 at 20°	—	9·9 at 20°
Succinic acid	−4·54	35·1 at −1°	−4·73	50·7 at −1°	−4·98	93·0 at −1°
,, ,,	—	19·0 at 21·5°	—	27·0 at 21·5°	—	41·0 at 21·5°
Benzoic acid	−2·88	7·6 at 3°	−2·74	6·6 at 3°	−2·97	6·8 at 3°
,, ,,	—	5·5 at 21°	—	4·9 at 21°	—	5·0 at 21°
Cinnamic acid	−3·80	22·4 at 0°	−3·70	20·6 at 0°	−3·79	23·2 at 0°
,, ,,	—	16·0 at 19·5°	—	14·6 at 19·5°	—	16·0 at 19·5°
Salicylic acid	−2·51	10·6 at −3°	−2·06	8·3 at −3°	−2·56	8·8 at −3°
,, ,,	—	6·9 at 21°	—	5·6 at 21°	—	6·1 at 21°

were made in the calorimetric bomb, the modification previously described being used in the case of the halogen compounds.

	Heat of combustion.		Heat of formation.
	Constant volume.	Constant pressure.	
Terebenthene	+1488·6 Cal.	+1490·8 Cal.	+4·2 liq.
Citrene	+1471·1 ,,	+1473·3 ,,	+21·7 ,,
Camphene hydrochloride	+1467·6 ,,	+1469·8 ,,	+64·5 cryst.
Terpilene dihydrochloride	+1465·5 ,,	+1467·7 ,,	+105·9 ,,
Terebenthene hydrochloride	+1467·0 ,,	+1469·2 ,,	+65·1 ,,

The heat of combustion of citrene is practically the sum of that of cymene and hydrogen, and hence the union of the two latter to form citrene would develop no heat. It follows that citrene and its isomerides are not cymene hydrides, and do not belong to the benzene series, but are more easily converted into the latter the smaller the thermal disturbance that the change involves.

The heat of formation of citrene is practically identical with that of camphene (22 Cal.), and the conversion of terebenthene into camphene would develop +18·6 Cal. and into citrene +17·5 Cal. This great development of heat does not result from an alteration in molecular weight or in chemical function, but from an increase in the stability of the system.

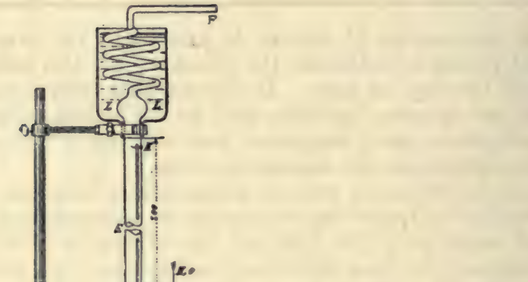
The formation of camphene hydrochloride from crystallised camphene and gaseous hydrogen chloride develops +21·7 Cal., a value somewhat greater than that for amylene hydrochloride (+17·6). The formation of the terpilene dihydrochloride from liquid citrene, and the gas develops +40·2 Cal., which gives practically the same value for each molecule of hydrogen chloride. The formation of terebenthene hydrochloride under similar conditions develops +38·9 Cal., the thermal disturbance being made up of the heat liberated by the conversion of the terebenthene into the camphene type (418·6 Cal.), and its subsequent combination with hydrogen chloride, the latter change developing +20·3 Cal.

Calorimetric experiments on the direct saturation of these hydrocarbons with hydrogen chloride are very difficult, but the results agree well with those obtained by combustion. The heat of dissolution of citrene dihydrochloride in citrene is −4·65 Cal., and the heat of dissolution of terebenthene hydrochloride in terebenthene is −0·75 Cal. The excess of heat developed by the action of hydrogen chloride on terebenthene is not due to the crystallisation of the product, but to a partial conversion of the terebenthene into a camphene. C. H. B.

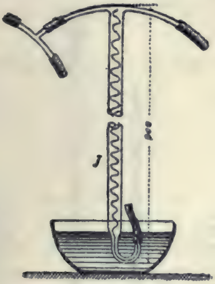
Atomic Weights and the Densities of Liquids. By A. Moulin (*Compt. rend.*, **112**, 1209—1211).—This paper contains a number of calculations in which the author endeavours to show that "the product of the atomic weight of a liquid substance into its density is the sum of the corresponding products of its elements."

C. H. B.

Study of Evaporation. By C. SCHALL and L. KOSSAKOWSKY (*Zeit. physikal. Chem.*, **8**, 158—182 and 241—271).—The apparatus employed by the authors is that shown in the figure. The retort *A* holds the liquid under examination, which is heated by the vapour of the same liquid contained in the vessel *B*. The tube *E*, ending in the globe *LL* and worm, serves as a condenser for the vapour of the liquid in *B*, and in this is placed the thermometer which indicates the temperature of the vapour, and consequently also that to which *A* is heated. The tube *C* leads from the retort *A* to the bent tubes 1, 2, 3, and 4, which form a siphon arrangement to two ⋃-tubes. The short tube *O* connects *C* with the end *G* of the siphon tubes, and serves to establish a uniform pressure in the whole system, and is also used for filling the retort by means of the tap funnel *s*. The condensation of the vapour which passes through the tube *C* is effected by surrounding this with the vessel *M*, which is kept filled with water of a definite temperature, or, if necessary, with a mixture of snow and salt. The tube *G* ends in the Bunsen valve at *V*, which serves to



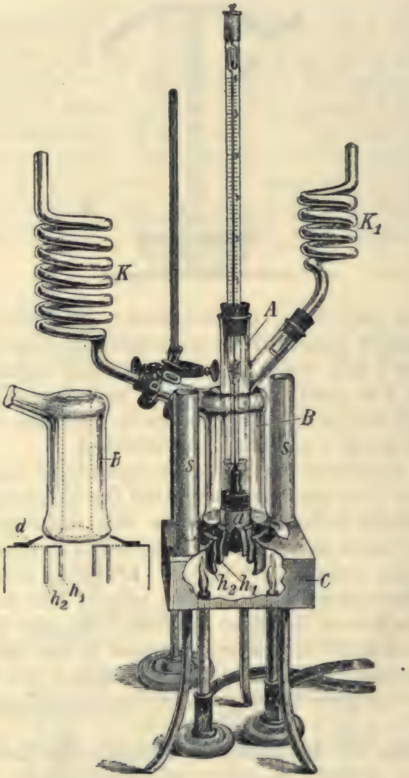
keep the pressure in the interior of the apparatus constant. When working under reduced pressure, both *V* and *F* are connected by means of a ┳-tube and manometer *J* with the air-pump, and any desired pressure can then be obtained. The temperature of the siphon tubes is kept constant by surrounding them with water, and that of the tubes 3 and 4 can be ascertained by means of the thermometer *W*. Tube 4 is carefully calibrated and divided into millimetres, and the rise of liquid in this tube serves to measure the amount which passes over in a given time from the retort *A*.



Experiments were made with a large number of organic compounds. The results show that the times required for the evaporation of equal weights of different substances under the same pressure, near the ordinary boiling point and with a constant fall in tension, are inversely proportional to the molecular weights. Only the first members of the alcohol series form exceptions to this rule. The most probable explanation of the above relation is found in the behaviour of the diffusion coefficients, which, when reduced to the above experimental temperatures, pressure (760 mm.), and volume, are found to be proportional to the absolute boiling points under atmospheric pressure.

H. C.

Determination of Molecular Weights by the Boiling Point Method. By E. Beckmann (*Zeit. physikal. Chem.*, **8**, 223—228).—The difficulty in accurately determining the boiling point of a solution increases with the difference of temperature which exists between the heated liquid and the outside air. This may be overcome by surrounding the liquid containing the solution by an outer vessel containing the solvent and kept at the boiling temperature. The inner vessel A, which contains the solution, is of the same form as that used in the freezing point determinations (this vol., p. 784); it is 25 mm. wide, with platinum wire sealed into the bottom and filled to a height of about 35 to 40 mm. with glass beads (Abstr., 1890, 323). This is surrounded by the vessel B, containing about 20 c.c. of the solvent, which is to act as a jacket to A. The two vessels are kept from actual contact by means of the asbestos paper *a*, and both are connected with reflux condensers K_1 and K. The thermometer used in the determinations is inserted in A, and is similar to that described in the former paper (*loc. cit.*). The chamber C, which is constructed of asbestos cardboard, is heated by means of ordinary Bunsen burners, and the apparatus itself is protected from the direct action of the flame by the asbestos rings h_1 and h_2. S, S serve to carry off the products of combustion. Direct heating of the solutions is only necessary in the case of water, when a small flame, which does not actually come into contact with the vessels A and B, may be used. In all other cases the heat transferred from C is sufficient to raise the solution even in the inner vessel to the boiling point. The outer vessel B may be made of either glass or copper. Experiments with this apparatus are quoted, showing that it gives correct results in molecular weight determinations. H. C.



Influence of Alkaline Bases on the Solubility of Alkaline Salts. By ENGEL (*Compt. rend.*, **112**, 1130—1132).—When sodium hydroxide is added to a solution of sodium chloride saturated at 0°, one equivalent of the hydroxide precipitates half an equivalent of the salt, or 1 mol. of the salt is precipitated for each molecule of the anhydrous oxide, Na_2O, added. At first, the sum of the molecules is a little lower, but afterwards it is a little higher, than would be the case if the law were exactly true. Sodium hydroxide behaves in a similar manner with solutions of sodium nitrate, and potassium hydroxide precipitates potassium bromide, iodide, or nitrate according to the same approximate law. Ammonia, on the other hand, increases the solubility of ammonium chloride, a result doubtless due to the formation of the double compound described by Troost. C. H. B.

Influence of Potassium Salts on the Solubility of Potassium Chlorate. By C. BLAREZ (*Compt. rend.*, **112**, 1213—1215).—Saturated solutions of potassium chlorate, when mixed with solutions of potassium hydroxide or other potassium salts, deposit part of the chlorate. The sum of the quantity of the chlorate remaining in solution and the potassium in the salt added remains constant, this sum being equal to the weight of chlorate that would be dissolved in pure water at the particular temperature. Potassium chlorate, therefore, behaves in the same manner as other potassium salts. C. H. B.

Magnitude of the Pressure in Co-existing Phases of Mixtures, especially in Salt and Acid Solutions. By J. D. VAN DER WAALS (*Zeit. physikal. Chem.*, **8**, 188—214).—An application of the results obtained in a former paper (Abstr., 1890, 556) to the case of dilute solutions. The author arrives at the conclusion that it is necessary to assume the occurrence of the dissociation of electrolytes in dilute solutions, but that there is a certain specific attraction between the solvent and dissolved substance which should also be taken into account. H. C.

Change of Colour of Salt Solutions. By D. ISAACHSEN (*Zeit. physikal. Chem.*, **8**, 145—149).—According to Wiedemann, the well-known colour change which takes place on heating a solution of cupric chloride is due to the existence of different hydrates at different temperatures, and is accompanied by a change of direction in the curve for the electrical conductivity of the solution. The author has examined a solution containing 13·1 per cent. $CuCl_2,2H_2O$, the colour of which changes from blue to green at about 60°. The conductivity was determined for temperatures between 11·6° and 74°. The results, when plotted against the temperatures, give a uniform curve, the conductivity at any temperature being given by $\lambda_{t^\circ} = \lambda_{20_\circ}[1 + 0·01841(t - 20) - 0·0000405(t - 20)^2]$. No sudden change of any kind is observed at the point corresponding with the colour change. Similar results were obtained with a solution of cobalt bromide containing 21·8 per cent. $CoBr_2$. From this the author concludes that the electrical conductivity of the solution affords no clue to the cause of the colour change.

In order to ascertain whether the dissociation theory affords any explanation of the phenomena, solutions of the above salts were also examined both by the freezing point and vapour pressure methods. The molecular reductions obtained by the two methods were the same in both cases, so that no conclusion is to be arrived at by this means. H. C.

Theory of Double Linkage. By Z. H. Skraup (*Monatsh.*, **12**, 146—150).—In a double linkage, the two bonds may have either an equal or an unequal value. Against the latter assumption, there is the case of the production of tartaric acid from maleïc and fumaric acids, whilst the former is not in keeping with the fact that in additive reactions only one of the bonds of a double linkage is broken. We should have then to assume that the two bonds are at the same time both equal and unequal. This apparent contradiction becomes intelligible if we take into account the internal motion of the atoms within the molecule. In ethane, the two carbon atoms may be regarded as approaching and receding from one another along the line representing their bond of union. In ethylene, on the other hand, the motion of the carbon atoms towards one another may be supposed to take place in the direction of each bond of union alternately, so that as they are approaching one another in the one direction, they are receding from one another in the other. Each bond of union would thus become alternately the stronger and the weaker. Among a large number of molecules, such as those of maleïc acid, to each phase in the one direction there will be a corresponding one in the other, so that by the addition of two unlike elements or groups, equal numbers of unlike molecules will result; hence, for instance, the production of inactive malic acid. The motion which is here assumed will depend not only on outside influences, such as that of temperature, but also on the intramolecular, chemical attractions, and in this we have an explanation for the fact that some unsaturated compounds undergo additive change readily and others only with difficulty.

H. C.

Inorganic Chemistry.

Preparation of Hydrobromic Acid. By W. Feit and K. Kubierschky (*J. Pharm.* [5], **24**, 159—160; from *Pharm. Zeit. Russ.*, **30**, 298).—Although concentrated sulphuric acid decomposes potassium bromide with liberation of bromine, when a more dilute acid is used there is no evolution of bromine. To obtain pure hydrobromic acid, 150 c.c. of sulphuric acid of 1·41 sp. gr. is poured on to 100 grams of coarsely-powdered potassium bromide, and the mixture warmed gently and shaken until the salt is dissolved. The liquid is then submitted to distillation; it begins to boil at about 126°, and the temperature slowly rises to 150°, at which point almost the whole of the hydrobromic acid passes over; then the temperature rapidly goes up to 200°, and traces of sulphuric acid are mechanically carried over. The process is now stopped, as between 200° and 250° only small quantities of hydrobromic acid, mixed with a little sulphuric acid, pass over. The distillate is redistilled, collecting only what passes over at 126°; this has a sp. gr. of 1·49, contains 48 per cent. of HBr, is colourless, and contains neither sulphuric acid, sulphurous acid, nor bromine. 150 grams of bromide yield about 200 grams of acid. If the bromide contains bromate, the receiver is changed when the distillate becomes colourless; the acid thus obtained containing bromine is treated with a little sodium sulphite and rectified with the rest. Gaseous hydrobromic acid may be obtained by distilling the solution containing 48 per cent. from anhydrous calcium bromide.

J. T.

Diammonium Semisulphate, $(N_2H_4)_2,H_2SO_4$. By T. CURTIUS (*J. pr. Chem.* [2], **44**, 101—102).—The hydrazine sulphate, N_2H_4,H_2SO_4, described in previous communications (Curtius and Jay, Abstr., 1889, 340; Curtius and Schulz, this vol., p. 263) is not the normal but the acid sulphate of hydrazine.

Diammonium semisulphate, $(N_2H_4)_2,H_2SO_4$, the normal salt, is obtained when hydrazine hydrate is neutralised with sulphuric acid, and the solution, after concentration, evaporated to dryness in a vacuum. It crystallises in large, glassy, flat, anisotropic prisms, melts at 85°, is extremely deliquescent, has a neutral reaction, and is precipitated from its aqueous solutions as an oil on the addition of alcohol, in which it is insoluble. The addition of a crystal of the salt and rubbing with a glass rod causes the oily sulphate to become crystalline.

W. P. W.

Electrolysis of Fused Compounds of Boron and Silicon. By A. MINET (*Compt. rend.*, **112**, 1215—1218).—Sodium chloride (60 parts) is mixed with sodium aluminium fluoride (30 parts), and to this mixture at the moment of fusion is added silica (5 parts) and alumina (5 parts). The mass is kept fused at 700—1000° in an iron crucible, lined with carbon, which serves as the cathode. The anode consists of compressed carbon. The nature of the product depends on the composition of the bath and the strength of the current. Some of the products had the following composition:—

Al	95·5	98·4	97·67	96·80	92·60	89·80	93·40
Si......	0·33	1·33	1·74	1·60	6·10	8·90	1·00
Fe	0·17	0·63	0·59	1·60	1·30	1·57	6·66

The alloy containing the highest proportion of silicon has a tensile strength greater than that of pure aluminium.

If boric anhydride is substituted for the silica, alloys of aluminium and boron are obtained, in which the proportion of boron may rise to as much as 80 per cent. The alloy is easily separated from the excess of aluminium by the action of sodium hydroxide.

C. H. B.

Sodium and Potassium Nitrite. By H. N. WARREN (*Chem. News*, **63**, 294).—A very sensitive surface of spongy platinum is obtained by soaking asbestos yarn in a solution of platinum oxalate, made by heating freshly prepared platinic chloride at 400° F., until no more chlorine is evolved, then boiling the residue with a slight excess of sodium carbonate, finally dissolving it in oxalic acid, and concentrating the solution. The soaked asbestos yarn, after drying and igniting, is exposed to a current of ammonia and air in a combustion tube, the remote end being heated by a Bunsen to start the reaction; the whole platinised surface soon becomes intensely hot, while dense clouds of ammonium nitrite rapidly form, and are conducted into sodium or potassium hydroxide, where the corresponding nitrite is formed, the evolved ammonia being used for producing a further supply of ammonium nitrite. D. A. L.

Silver Subchloride. By GUNTZ (*Compt. rend.*, **112**, 1212—1213).—Silver subchloride or argentous chloride, Ag_2Cl (this vol., p. 983), varies in colour from deep violet-red to violet-black; exposure to sunlight tending to convert it into the latter modification, without loss of chlorine. When heated, it splits up into argentic chloride and metallic silver. It is not attacked by dilute nitric acid, but when warmed with the concentrated acid, it is converted into argentic chloride, mixed with a varying proportion of argentous chloride, forming the coloured products described by Cary Lea (Abstr., 1888, 1). Potassium cyanide decomposes it in accordance with the equation $Ag_2Cl + 2KCy = Ag + AgCy + KCl$, and the heat of formation was determined by means of this reaction. $Ag_2 + Cl = Ag_2Cl$ develops +29·7 Cal., whilst $Ag + Cl = AgCl$ develops +29·2 Cal., a difference similar to that observed in the case of the two fluorides. $2AgCl = Ag_2Cl + Cl$ would absorb −28·7 Cal.

C. H. B.

Some Physical Properties of Nickel Carbon Oxide and of other Nickel Compounds. By L. MOND and R. NASINI (*Zeit physikal. Chem.*, **8**, 150—157).—The vapour of nickel carbon oxide burns in the air with a strongly luminous flame, which appears smoky in consequence of the separation of metallic nickel. This flame gives only a somewhat brilliant continuous spectrum. In a Geissler tube, the vapour of the compound gives the spectrum of carbon monoxide only.

The molecular weight of the compound was determined by the cryoscopic method in a benzene solution. The value found was 176·5 instead of 170·6, the theoretical number.

The sp. gr. and coefficients of expansion of the liquid between 0° and 36° were also measured. The sp. gr. at 0° is 1·35613, at 36° 1·27132, the unit being water at 4°. The mean coefficient of cubic expansion between 0° and 36° is 0·001853, which is higher than that of most organic or inorganic compounds. The sp. gr. at the boiling point is 1·25406, and hence the molecular volume is 136·04. The critical temperature calculated from the formula of Thorpe and Rücker is 151°.

The refraction was measured for the hydrogen lines α, β, and γ, and for the lithium, sodium, and thallium lines. The compound is found to have a very strong dispersion, greater when calculated by Ketteler's formula, and slightly less by Gladstone's, than that of carbon bisulphide. The atomic refraction of nickel in this compound is found to be exceedingly high, at least three times greater than that calculated from observations made with other nickel compounds. This fact is in keeping with the view that the valency of nickel in nickel carbon oxide is greater than in its other compounds, and confirms the opinion derived from the study of the other properties of this substance that in it the nickel behaves as an octad element. H. C.

Action of Platinic Hydroxide on Tungstates. By A. ROSENHEIM (*Ber.*, **24**, 2397—2400).—The author has made the experiments described below to ascertain the course of the reaction between platinic hydroxide and tungstates, and also to throw further light on the nature of the compounds obtained by Gibbs (Abstr., 1877, 847).

Platinic hydroxide is prepared by boiling a solution of platinic chloride in hydrochloric acid with an excess of sodium hydroxide solution, and, after concentrating, neutralising with acetic acid, the precipitate being washed with water containing acetic acid; it generally contains a small quantity of alkali salt. The yield is not a good one, as much of the platinum remains in solution.

When a solution of a pure paratungstate is boiled with platinic hydroxide, according to Gibbs' directions (*loc. cit.*), a large portion of the latter dissolves, forming a deep-red liquid; when the two compounds are heated together in a sealed tube at 250—300°, somewhat more platinic hydroxide is dissolved, and a deep brownish-red liquid is formed, but in neither case could Gibbs' compounds be isolated, the reagents separating out uncombined. As Gibbs does not give analytical data, the nature of his compounds cannot be suggested, but it may be that they consisted of paratungstates containing mechanically occluded platinic hydroxide, coloured by partial reduction. Solutions of metatungstates dissolve platinic hydroxide in considerable quantities on boiling, and still more readily when heated in a sealed tube, although platinic hydroxide is quite insoluble in water, even when heated with it in a sealed tube at 300°; on evaporating these solutions, even under diminished pressure, nothing but the unaltered reagents was obtained. When a concentrated solution of normal sodium tungstate is boiled with platinic hydroxide, the solution becomes faintly yellowish, much less platinic hydroxide being dissolved than in the case of the acid salts; this is opposed to the view that platinic hydroxide acts as an acid. The strongly alkaline solution is filtered as quickly as possible, and, on cooling, a neutral compound, exhibiting the reactions of a paratungstate, separates from the filtrate in small yellow needles of the composition $5Na_2O,7WO_3,2PtO_2 + 35H_2O$; this cannot be recrystallised, as it then undergoes decomposition; on this account a further yield is not obtained by concentrating the mother liquor, and the compound cannot be prepared from dilute solutions of sodium metatungstate. It is a double salt of sodium paratungstate (1 mol.) and sodium platinate (2 mols.), as the following experiment proves. When the calculated quantities of sodium paratungstate and platinic hydroxide are boiled with sodium hydroxide solution, the same salt is formed, but this is not the case if sodium hydroxide is excluded.

It appears, therefore, that platinic hydroxide has very weak acidic properties (comparable with those of alumina), which it exhibits only with such alkaline salts as normal tungstates; it dissolves in para- or meta-tungstates as a base. A. R. L.

Atomic Weight of Bismuth. Composition of Commercial Bismuth and of Commercially Pure Bismuth. By R. SCHNEIDER (*J. pr. Chem.* [2], **44**, 23—48).—A controversial paper, in which the author warmly defends Marignac's determination of the atomic weight of bismuth from the criticisms of Classen (this vol., p. 525). Classen, in the same paper (*J. pr. Chem.* [2], **43**, 134), states that commercial bismuth contains several units per cent. ("ganze Procente") of copper, iron, and lead, and that purified bismuth procured from various sources also contains considerable quantities ("Procente") of these impurities. To show how misleading are these statements, the author quotes published analyses of commercial bismuth by v. Sill, Barth, and himself, and, in addition, has analysed samples of commercial and of commercially pure bismuth obtained from the smalt works of Saxony, since these furnish about three-fourths of the bismuth annually placed on the market, and may therefore be considered to supply the chief qualities of the metal met with in commerce. Two specimens of commercial bismuth from the smalt works, I, produced prior to October 1, 1890, and II, produced subsequent to that date, gave the following numbers:—

	Bi.	Ag.	Pb.	Cu.	Fe.	As.	S.	Total.
I.	99·791	0·070	0·084	0·027	0·017	—	trace	99·989
II.	99·745	0·066	0·108	0·019	trace	0·011	0·042	99·991

Three samples of bismuth sold as pure were analysed: III, purified from Johanngeorgenstadt metal by precipitation of the basic nitrate and subsequent reduction; IV, purified from Johanngeorgenstadt metal by precipitation of the oxychloride and subsequent reduction; V, purified from smalt works metal by precipitation of the oxychloride and subsequent reduction.

	Bi.	Ag.	Pb.	Cu.	Fe.	As.	Total.
III.	99·922	—	—	0·016	trace	0·025	99·963
IV.	99·849	0·047	0·049	0·019	trace	0·024	99·989
V.	99·892	—	0·065	0·032	trace	trace	99·989

With the object of determining to what extent impurities in bismuth are retained in the acid mother liquor when a nitric acid solution of the metal is precipitated by a known quantity of water, 10 grams of sample I were dissolved in some excess of nitric acid, and the solution stirred into 400 c.c. of water heated to 50°. The precipitate, after washing with distilled water, and drying at the temperature of a water-bath, weighed 6·5 grams; on analysis, the following numbers were obtained:—

	Bi.	Ag.	Pb.	Cu.	Fe.	Total.
VI.	9·9802	0·0070	0·0084	0·0027	0·0017	10·0000
VII.	5·2832	0·0069	0·0081	0·0025	0·0017	5·3024
VIII.	4·6960	—	0·0003(4)	0·0002(4)	—	4·6965
IX.	99·9893	—	0·0064	0·0043	—	100·0000

VI gives the composition of the metal employed, VII that of the solid constituents of the acid liquor, VIII that of the basic nitrate, and IX the percentage composition of the metal obtainable from it by reduction. W. P. W.

Compounds of Platinic Chloride with Hydrogen Chloride. By L. Pigeon (*Compt. rend.*, **112**, 1218—1220).—Red crystals of chloroplatinic acid, $H_2PtCl_6,6H_2O$, are dissolved in a small quantity of water and mixed with a large excess of concentrated sulphuric acid. A yellow precipitate forms which consists of deliquescent, microscopic crystals, acting strongly on polarised light; they have the composition $H_2PtCl_6,4H_2O$.

If chloroplatinic acid is heated at 100° in a vacuum in presence of fused potash, it melts in its water of crystallisation at about 60° bubbles of gas are evolved, and after two or three days at 100° a solid, crystalline, reddish-brown product remains of the composition $HPtCl_5,2H_2O$. When the latter is heated in a vacuum at 200°, in presence of fused potash, it loses the whole of its water and hydrogen chloride, and is converted into anhydrous platinic chloride, but the latter loses no chlorine so long as the temperature is kept below 220°. At 360°, half the chlorine is expelled and platinous chloride is obtained.

The decomposition of chloroplatinic acid would seem to indicate that it is really a hydrochloride of a chloride similar to those described by Engel, thus, $PtCl_4(HCl,2H_2O)(HCl,2H_2O),2H_2O$. It affords a further illustration of the importance of the crystalline hydrate $HCl,2H_2O$, obtained by Pierre and Puchot. C. H. B.

Luteorhodium Salts. By S. M. Jörgensen (*J. pr. Chem.* [2], **44**, 48—62).—When sodium roseorhodium pyrophosphate (Abstr., 1887, 114) is heated in quantities of about 10 grams at 110° for about a week, it becomes yellow and dissolves to a large extent in cold water with a yellow colour. The white, insoluble residue, after dissolution in water acidified with hydrochloric acid and precipitation with dilute nitric acid, gives a white, crystalline compound consisting of a mixture of nitratopurpureorhodium nitrate and luteorhodium nitrate, from which the latter can be separated by a tedious process described at length in the paper. Luteorhodium salts are very stable and can be prepared much more easily by heating chloropurpureorhodium chloride with concentrated aqueous ammonia. When 6 grams of the chloride is heated with 80 c.c. of 25 per cent. aqueous ammonia continuously for 24 hours at 100—102°, about 0·6 gram of the chloride remains unattacked and the product consists of 82·5 per cent. of luteo- and 17·5 per cent. of roseo-rhodium chloride; if the heating is continued for four days with quantities of 3—5 grams of the chloride, about 0·01 gram only remains unaltered, and the product consists of luteo-salt almost entirely free from the roseo-salt. The luteorhodium salts, as anticipated (*J. pr. Chem.* [2], **34**, 402), show considerable analogy to the roseo-salts, and in no case are differently coloured. As distinguishing characters, the conversion of the roseorhodium chloride, bromide, iodide, or nitrate into purpureo-salts on the one hand (see Abstr., 1887, 114) and the precipitation of the luteo-salts as the acicular normal orthophosphate on the other may be employed.

Luteorhodium nitrate, $(Rh,6NH_3)3NO_3$, on precipitation with dilute nitric acid, is obtained as a snow-white, crystalline powder consisting of small, rhombic prisms and aggregates; when crystallised from hot water, it forms larger crystals showing pyramidal faces, and on the addition of a large excess of concentrated nitric acid to the dilute solution, gives a voluminous precipitate consisting of needles frequently aggregated in six-rayed stars. It is converted into the chloride on repeatedly evaporating it to dryness with hydrochloric acid. One part of the salt dissolves in 48—49 parts of water at the ordinary temperature, and the reactions of the cold saturated solution with a number of reagents are given in the paper.

Luteorhodium chloride, $(Rh,6NH_3)Cl_3$, crystallises from its hot solution in concentrated hydrochloric acid in anhydrous forms, and may be obtained in rhombic tables, or not infrequently in compact needles, either by adding concentrated hydrochloric acid to its dilute aqueous solution or to that of the nitrate. It crystallises with 1 mol. H_2O in large, efflorescent forms when the neutral, aqueous solution is evaporated over sulphuric acid. It dissolves easily in water, and at 8° requires 7—8 parts for its solution. Digestion with hydrochloric acid for many hours at the temperature of the water-bath does not convert it into the chloropurpureorhodium chloride. The reactions of a 2 per cent. aqueous solution with a number of reagents are described.

Luteorhodium platinochloride, $2(Rh,6NH_3)Cl_3,3PtCl_4,6H_2O$, is obtained when neutral sodium platinochloride is added to a very dilute solution of the luteochloride, and the lustrous, tetragonal prisms which first separate are kept in contact with the mother liquor for some time. It crystallises in orange-yellow, hexagonal forms, is insoluble in water, and when dissolved in warm water containing hydrochloric acid, frequently crystallises from the solution in long needles of the composition $2(Rh,6NH_3)Cl_3,2PtCl_4,H_2O$ (dried at 100°), which are isomorphous with the corresponding cobalt and chromium salts; when washed with alcohol and treated with water, it decomposes into luteorhodium chloride and the original platinochloride.

Luteorhodium bromide, $(Rh,6NH_3)Br_3$, is prepared by adding hydrobromic acid to a solution of the nitrate or chloride. It crystallises in thin, almost regular, hexagonal tables, dissolves easily in water, although less readily than the chloride, and resembles the latter in its reactions.

Luteorhodium sulphate, $(Rh,6NH_3)_23SO_4,5H_2O$, is obtained when the chloride is decomposed by freshly precipitated silver oxide and water, and the strongly alkaline filtrate containing luteorhodium hydroxide in solution is rendered faintly acid with sulphuric acid, evaporated to one half on a water-bath, mixed with 60 per cent. alcohol until an opalescence is produced, and allowed to remain at the ordinary temperature for about 24 hours. It crystallises in long, colourless, lustrous needles, and dissolves in 43 parts of water at 20°. In its reactions, it resembles the nitrate.

Luteorhodium orthophosphate, $(Rh,6NH_3)PO_4,4H_2O$.—The 2 per cent.

solutions of the nitrate, chloride, bromide, and sulphate are not precipitated by ordinary sodium phosphate, but on the addition of ammonia an amorphous precipitate of the orthophosphate is obtained, which, in contact with the mother liquor, soon crystallises in long, lustrous needles.

Sodium luteorhodium pyrophosphate, $(Rh,6NH_3)_2(P_2O_7)_2Na_2,23H_2O$, is obtained as a silky, snow-white, crystalline precipitate on the addition of sodium pyrophosphate to very dilute solutions of the neutral luteorhodium salts. It crystallises in small, hexagonal prisms or rhombic tables, and is almost insoluble in water.

W. P. W.

Acid Luteorhodium and Roseorhodium Nitrates. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **44**, 63—66).—*Luteorhodium hydrogen nitrate*, $(Rh,6NH_3)3NO_3,HNO_3$, is obtained by adding to a solution of 1 gram of luteorhodium nitrate in 100 c.c. of water about 400 c.c. of concentrated nitric acid, filtering through pumice, washing once with concentrated nitric acid, then once with absolute alcohol, and finally drying in a current of dry air during 12—24 hours. It crystallises in long, colourless needles, and, like all the following salts, is decomposed into the normal nitrate by water and dilute alcohol.

Luteocobalt hydrogen nitrate, $(Co,6NH_3)3NO_3,HNO_3$, prepared in like manner, crystallises in orange-yellow needles, and, like the rhodium salt, does not lose nitric acid when powdered and mixed with absolute alcohol.

Luteochromium hydrogen nitrate, $(Cr,6NH_3)3NO_3,HNO_3$, like the following compounds, undergoes partial decomposition on treatment with absolute alcohol, and the washing with this reagent is therefore omitted in its preparation. It crystallises in lemon-yellow needles, and cannot be heated at 100° without decomposition.

Roseorhodium hydrogen nitrate, $(Rh,5NH_3,H_2O)3NO_3,HNO_3$, crystallises in colourless needles, and on titration by aqueous soda with litmus and with perfectly neutral silver nitrate solution as indicators, gives numbers indicating respectively the presence of one or two molecular proportions of nitric acid, a result due to the basic character of roseo-salts which render litmus blue, although they do not precipitate neutral silver nitrate.

Roseocobalt hydrogen nitrate, $(Co,5NH_3,H_2O)3NO_3,HNO_3$, crystallises in needles having the colour of the ordinary roseocobalt salts.

Roseochromium hydrogen nitrate, $(Cr,5NH_3,H_2O)3NO_3,HNO_3$, crystallises in needles having perhaps a colour slightly more yellow than that of the normal salts. W. P. W.

Mineralogical Chemistry.

Aguilarite, a new Species. By F. A. GENTH (*Amer. J. Sci.*, **41**, 401—403).—This interesting mineral was found by Mr. Aguilar, the Superintendent of the San Carlos mine, at Guanajuato, Mexico. The crystals are isometric, being skeleton dodecahedra with only the edges well developed. The colour is iron-black, fracture hackly, hardness 2·5, and sp. gr. 7·586. Analysis gave results in accord with the formula Ag_2S,Ag_2Se. B. H. B.

Seleniferous Bismuthinite and Guanajuatite. By F. A. GENTH (*Amer. J. Sci.*, **41**, 402—403).—A specimen received by the author as crystallised guanajuatite proves on analysis to be a seleniferous bismuthinite of the composition $4Bi_2S_3,Bi_2Se_3$. This result suggested a repetition of the analysis of guanajuatite with a specimen that came from an old German collection. The results of the analysis correspond with the formula $Bi_2S_3,2Bi_2Se_3$. It is probable that the same mineral has been analysed by Frenzel, and the existence of the species cannot be questioned. B. H. B.

Griphite, a new Phosphate from Dakota. By W. P. HEADDEN (*Amer J. Sci.*, **41**, 415—417).—The mineral described was found in the Riverton lode, near Harney City. It occurs in the granite in kidney-shaped masses, some of which weigh upwards of 50 lbs. The mineral has a sp. gr. of 3·401 and a hardness of 5·5. Carefully selected material gave on analysis the following results :—

P_2O_5.	MnO.	CaO.	Al_2O_3.	FeO.	MgO.	Na_2O.	K_2O.
38·52	29·64	7·47	10·13	4·00	0·15	5·52	0·30

H_2O.	Cl.	Insol.	Total.
4·29	0·11	0·16	100·29

From these results the author calculates the formula $P_2R'_5O_{10}$, which is a salt corresponding with normal phosphoric acid, and in it $R = (Mn, Ca, Fe, H_2, Na_2)\frac{3}{4} + Al\frac{1}{4}$. For this new phosphate the name of griphite is suggested, from γρῖφος (puzzle) in allusion to its unusual and somewhat enigmatical composition.

The author also describes a phosphate occurring in nodules in the granite of the Nickel Plate tin mine, Dakota. The mineral is dark-green, has a hardness of 5, and a sp. gr. of 3·612. On analysis, it yielded results from which the author calculates the formula $4R'_3PO_4 + 9R''_3P_2O_8$, showing that the mineral cannot be regarded as identical with triphylite. B. H. B.

Alunite and Diaspore from Colorado. By W. CROSS (*Amer. J. Sci.*, **41**, 466—475).—The occurrences described by the author lie between the mining towns of Silver Cliff and Rosita, in Custer Co., Colorado, of which district a sketch of the geology is given. The area is regarded by the author as practically a volcano, with two vents in particular, which became true solfataras, and about them the rhyolite has been altered at the one, Democrat Hill, to an alunite rock, and at the other, Mt. Robinson, to an alunite-diaspore rock. In the latter locality, there occurs a rough, finely cellular rock, consisting of bluish quartz and a transparent, colourless mineral in irregular grains. This mineral, at first supposed to be alunite in an unusually pure state, was analysed and found to be diaspore, a result confirmed by a study of its physical and optical properties. There is but little evidence upon which to base a theory as to the origin of this mineral; but it seems probable that it is here a result of the destruction of alunite. B. H. B.

Columbite of the Black Hills, Dakota. By W. P. Blake (*Amer. J. Sci.*, **41**, 403—405).—The specimens of columbite collected by the author in 1884 have been preserved with the intention of preparing a full description as soon as the chemical investigation could be completed. As the numerous analyses published by W. P. Headden (this vol., p. 886) supply this want, the author now gives the results of a crystallographic study of the specimens. Some of the principal measurements for the identification of the faces are given, and for comparison the calculated angles obtained from the axial ratio established by E. S. Dana, $a : b : c = 0·8285 : 1 : 0·88976$.

B. H. B.

Polycrase of North and South Carolina. By W. E. Hidden and J. B. Mackintosh (*Amer. J. Sci.*, **41**, 423—425).—The occurrence and composition of this mineral were recently announced by the authors (Abstr., 1890, 854). Their later attempts in the separation of the metallic acids have given more satisfactory results, as the initial fusion was made with potassium hydrogen sulphate, and not with the sodium salt previously used. The results have enabled the authors to identify the mineral as polycrase, and to deduce for the species the formula

$$3(Nb_2O_5,5TiO_2),10(2RO + H_2O),$$

or, if H_2O is grouped under the general head of RO, the simple form $Nb_2O_5,5TiO_2,10RO$.

It is evident that this mineral is not merely an isomorphous mixture of a niobate and a titanate, but that it is a definite salt of a complex inorganic acid, a niobo-titanate. The discovery, by the aid of the spectroscope, of the presence of scandium in this polycrase adds to its interest. B. H. B.

Axinite, Eudialyte, Titanite, and Monticellite. By F. A. Genth, S. L. Penfield, and L. V. Pirsson (*Amer. J. Sci.*, **41**, 394—400).—1. *Axinite.*—The authors describe three new varieties of this mineral. The first variety is found as a great rarity at Franklin, New Jersey. The crystals are of a yellow colour, and are of interest, as they have a very unusual habit and possess some rare planes. On analysis, the crystals yielded—

Ignition.	SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	CuO.	ZnO.	MnO.	MgO.	CaO.	Total.
0·76	42·77	5·10	16·73	1·03	0·12	1·48	13·69	0·23	18·25	100·16

The mineral therefore contains a higher percentage of manganese than has ever before been observed.

The second variety described was obtained from Guadalcazar, Mexico, where it is found in minute crystals associated with white felspar. The colour is sage-green, and the sp. gr. 3·299. The crystals are tabular, with curved or uneven faces. Analysis gave the following results:—

Ignition.	SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	CuO.	MnO.	MgO.	CaO.	Total.
0·75	42·85	5·17	16·96	5·00	0·19	9·59	0·87	18·49	99·87

The last variety, from McKay's Brook, consists of very small, brown, tabular crystals, arranged so as to form a somewhat columnar, granular rock.

2. *Eudialyte.*—The authors describe crystals of eudialyte from Magnet Cove, Arkansas. The description is in accord with that given by J. F. Williams in 1890.

3. *Titanite.*—One of the rarer minerals of Magnet Cove is titanite. It occurs in small, brown crystals giving on analysis the following results:—

Ignition.	SiO_2.	TiO_2.	FeO.	MgO.	CaO.	Total.
0·57	30·84	39·35	0·73	trace	28·26	99·75

4. *Monticellite.*—Among the minerals from Magnet Cove, the very rare species monticellite has been discovered. The crystals are characterised by the development of the brachypinacoid and of the brachydome $2P\breve{\infty}$, and in these respects they differ from those of European localities. On analysis, the mineral yielded results corresponding with the formula $(Mg,Mn,Fe)_2SiO_4,Ca_2SiO_4$. B. H. B.

Organic Chemistry.

Calculation of the Melting and Boiling Points of Normal Paraffins. By J. Hinrichs (*Compt. rend.*, **112**, 1127—1130).—The author shows that the melting and boiling points of the normal paraffins calculated by means of his formula (*Compt. rend.*, **112**, 998) agree well with the actual determinations made by Krafft.

C. H. B.

Isomeric Change in Unsaturated Hydrocarbons. By A. Favorsky (*J. pr. Chem.* [2], **44**, 208—238).—The scheme proposed by the author (*J. pr. Chem.* [2], **37**, 382) to explain the isomeric change of mono-substitution derivatives of acetylene into di-substitution derivatives by the action of alcoholic potash finds an exception in the case of allylene. When the latter is treated with alcoholic potash, ethylisopropenyl ether, a compound which does not yield isoallylene under the ordinary conditions, is obtained. The cause of this appeared at first to be that isoallylene is gaseous, and must consequently develop a much higher vapour tension when heated than the liquid derivatives; this tension on reaching a certain limit would prevent the further dissociation of the ether. According to this view, the ether when heated ought to undergo partial dissociation into isoallylene; this is not the case, however, the compound remaining unaltered when heated in a sealed tube at 100—200° either by itself, or with concentrated alcoholic potash or potassium hydroxide moistened with alcohol. The hypothesis that there is a tendency for the formation of methyl groups is borne out by experiment (see below), whilst the fact that isoallylene could only be formed from ethylisopropenyl ether by the removal of hydrogen from a methyl group explains the stability of the latter.

Isoallylene was prepared by Gustavson and Demianoff's method (Abstr., 1889, 29); it only contained slight traces of allylene, if any. When an alcoholic solution of isoallylene (prepared at 0°) is heated with alcoholic potash in a sealed tube at 160—170° for 12 hours, the residual gas appears to contain more allylene than before the experiment, which is perhaps due to the circumstance that the latter is less easily attacked by the alkali than isoallylene, whilst the same ethylisopropenyl ether is formed as in the case of allylene (see above).

When the so-called diallyl (b. p. 60°), prepared according to Berthelot and Lucas' directions (*Compt. rend.*, **42**, 233), is heated in a sealed tube with alcoholic potash for six hours at 170°, and the portion of the product boiling below 85° is again heated with alcoholic potash for the same time at 200°, this being repeated, an isomeric hydrocarbon boiling at 80—85° is obtained, together with a small quantity of a substance boiling at 202°. This hydrocarbon (b. p. 80—85°) is dissolved in twice its volume of dry ether and treated with bromine (2 mols.) at 0°. The mixture is placed in the dark for 24 hours, then poured into a dish, the ether allowed to evaporate, and the liquid portion of the residue removed by treating it with absolute alcohol (see below), the solid portion being crystallised from benzene; it melts at 140—160°. The finely powdered substance is shaken with successive portions of light petroleum, whereby a compound melting at 180° remains, whilst a crystalline product melting at 107° is obtained on evaporating the petroleum. When the above-mentioned alcoholic solution is diluted with water, and the precipitated oil placed over concentrated sulphuric acid, crystals separate after several days; these are freed from the liquid by treatment with 60 per cent. alcohol, crystallised from ether, and identified as diallyl tetrabromide melting at 63°. The 60 per cent. alcohol solution is then evaporated, and the oily residue dried over concentrated sulphuric acid; it decomposes when distilled under a pressure of 30 mm. This liquid and the two above-mentioned solid products are tetrabromides of the composition $C_6H_{10}Br_4$; 80 grams of the diallyl yield 5 grams of the liquid, an equal weight of the compound melting at 180°, and 1 gram of that melting at 107°. When, therefore, diallyl is treated with alcoholic potash, three isomerides are produced whose constitution is uncertain, the more so as observations tend to show that the diallyl itself is not a homogeneous substance (compare Ciamician and Anderlini, Abstr., 1890, 20).

Diisobutenyl, $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$, is prepared according to Przibytek's directions by treating isobutyl chloride with metallic sodium; it boils at 115—116° (783 mm.). When heated at 180° in a sealed tube, diisobutenyl yields an isomeric hydrocarbon boiling at 134—135° (768·8 mm.); this solidifies when cooled to 0°, and then melts at 7°. It appears to be identical with Przibytek's diisocrotyl, $CMe_2\colon CH\cdot CH\colon CMe_2$, and the formation of the latter is in harmony with the author's hypothesis that there is a tendency to the formation of methyl groups.

Dipropargyl is prepared according to Henry's directions (Abstr., 1873, 1215). Diallyl tetrabromide (320 grams) is triturated with a large excess of pulverised caustic alkali, and distilled on a sand-bath, whereby a heavy oil (146 grams) is obtained. This, on distillation over calcium chloride, commences to boil at 80°, and the temperature gradually rises to 150°, at which it begins to decompose; the distillation is then continued under a pressure of 40 mm. When the distillate, consisting of the crude mixture of dipropargyl and bromides, is heated on the water-bath in a reflux apparatus for five hours with a large excess of alcoholic potash, and the product fractionated, unaltered dipropargyl passes over at first, whilst Griner's dimethyldiacetylene, $CMe\colon C\cdot C\colon CMe$ (Abstr., 1887, 1033), melting at 65°, is obtained from the portion boiling at 120—140°. The same compound is produced from pure dipropargyl and alcoholic potash, together with a compound of the formula $C_8H_{12}O$. A. R. L.

Polymeride of Trichloracetonitrile. By N. Tscherwen-Iwanoff (*J. pr. Chem.* [2], **44**, 160).—Weddige (Abstr., 1886, 323) showed that trichloracetonitrile is polymerised by the action of dry hydrogen chloride and prolonged exposure to light. By using hydrogen bromide, the author effected the change in 36 hours, the identity of the polymeride being determined by its melting point (96°) and by analysis.

When Weddige's amidoperchloromethylcyanidine is heated with hydrochloric acid, it yields chloroform, ammonia, and dihydroxyperchloromethylcyanidine, $C_3N_3(OH)_2\cdot CCl_3$ (m. p. 152—153°), and when it is acted on by zinc-dust, it yields *amidodimethylcyanidine*, $C_3N_3Me_2\cdot NH_2$, which crystallises in long needles and melts at 170°. A. G. B.

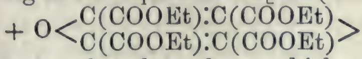
Oxidation of Sodium Alkyloxides by Atmospheric Oxygen. By F. v. Hemmelmayr (*Monatsh.*, **12**, 151—159).—When sodium methoxide is exposed to dry air at temperatures between 100° and 150°, it is in part oxidised to sodium formate and water; the water thus liberated acts on a further quantity of the methoxide, forming sodium hydroxide and methyl alcohol. Another molecule of the methoxide is oxidised in presence of the sodium hydroxide with the production of water and sodium carbonate.

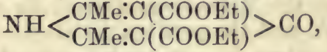
Sodium ethoxide and sodium amyloxide behave like sodium methoxide, giving the corresponding fatty acids, that is, acetic and valeric acids respectively. In those cases where the temperature at which the oxidation occurred was raised above 200°, much carbonic acid and traces of oxalic acid and of formic acid were formed. In no case was the quantity of fatty acid produced more than 50 per cent. of that theoretically obtainable from the alkyloxide. G. T. M.

Diethylenediamine (Piperazine). By A. Ladenburg (*Ber.*, **24**, 2400—2402).—*Nitrosopiperazine*, $C_4H_8N_2(NO)_2$, is obtained when sodium nitrite is added to a solution of piperazine hydrochloride, and the mixture heated for a short time. The product, when collected and purified by crystallisation from boiling water, forms yellowish, lustrous plates, melts at 158°, and is sparingly soluble in cold water and in ether, readily in boiling water and hot ether. It is not decomposed by boiling sodium hydroxide solution, or by concentrated sulphuric and hydrochloric acids at the ordinary temperature. It gives a deep-blue coloration, after some minutes, with a solution of phenol in concentrated sulphuric acid.

γ-Dimethylpiperazine, $C_4H_8N_2Me_2$, is formed when an aqueous solution of piperazine is heated for several hours in a reflux apparatus with an excess of potassium methyl sulphate, until the mixture is no longer alkaline, and ceases to give the nitroso-reaction. An excess of sodium hydroxide is then added, and the product distilled as long as the base passes over; the distillate is evaporated with hydrochloric acid, and the *hydrochloride*, $C_6H_{14}N_2,2HCl$, thus obtained, crystallised from alcohol. It forms lustrous prisms, which lose their lustre at 100°, and develop the odour of the base; it appears also to lose water of crystallisation, and to dissociate at this temperature. The *platinochloride*, $C_6H_{14}N_2,H_2PtCl_6$, separates from boiling concentrated hydrochloric acid in small, lustrous prisms. The *cadmioiodide*, $C_6H_{14}N_2,2HI,CdI_2$, crystallises from boiling water in colourless, thick prisms. The *aurochloride*, the *bismuthoiodide*, and the *periodide* are sparingly soluble, crystalline compounds. The *base* is easily volatile, and has a penetrating odour recalling that of methylamine.

A. R. L.

Synthesis of Pyrone. By A. Peratoner and B. Strazzeri (*Gazzetta*, **21**, 283—312).—I. *Action of Carbon Oxychloride on Copper Oxalacetate.*—It was supposed that these substances would react according to the equation $Cu[CH(COOEt)\cdot CO\cdot COOEt]_2 + COCl_2 = CuCl_2$  $+ \mathrm{O}<\begin{matrix}\mathrm{C(COOEt)\colon C(COOEt)}\\ \mathrm{C(COOEt)\colon C(COOEt)}\end{matrix}>\mathrm{CO} + H_2O$, yielding an ethyl pyronetetracarboxylate, from which pyrone or chelidonic acid might be obtained by hydrolysis. On mixing, however, a benzene solution of carbon oxychloride with copper oxalacetate, and allowing it to remain for about a month, the copper salt takes up an appreciable quantity of chlorine. On treating the product with dilute sulphuric acid, pyruvic acid and a small quantity of a chlorinated derivative of pyruvic acid are formed. The latter compound yields a *hydrazone*, $CH_2Cl\cdot C(COOH)\colon N_2HPh$, which crystallises in short, flattened, yellow needles, melts at 199—200°, and dissolves readily in organic solvents and in sodium carbonate, but only very sparingly in water. On heating to 220°, it evolves carbonic anhydride, and the previously fused mass resolidifies. On treating an aqueous solution of the residue with dilute potash, a small quantity of a substance separates, crystallising in small, white, lustrous needles, melting at 110—111°. It has feeble basic properties, dissolves in dilute acids and in organic solvents, but only sparingly in water, with which it forms an alkaline solution. No analysis could be made, but it was ascertained to be free from chlorine.

II. *Formation of Ethyl Dimethylpyronedicarboxylate.*—In order to prepare this, sodium (6 grams) is added to a solution of ethyl acetonedicarboxylate (20 grams) in dry ether (20 c.c.), and heated on the water-bath for two hours. Any unaltered sodium is then withdrawn, dry ether (150 c.c.) added, and dry acetic chloride (12·8 grams) quickly introduced. The action is energetic, and when it is completed the liquid is cooled, shaken with water, and the ethereal solution dried over calcium chloride, and evaporated. The product is ethyl dimethylpyronedicarboxylate, and crystallises from boiling ether in large, colourless, tabular crystals, melts at 79—80°, and is generally identical with the compound prepared by Conrad and Guthzeit (Abstr., 1886, 333), and yields an identical *lutidone* derivative,  $NH<\substack{CMe{:}C(COOEt)\\CMe{:}C(COOEt)}>CO$, melting at 220°.

A *disodium derivative* of ethyl acetonedicarboxylate is formed by treating a solution of the ethyl salt (10 grams) in benzene (3 to 4 vols.) with fragments of sodium (4 grams), and heating on the water-bath for 2 to 2½ hours. The reaction is completed when a reddish tinge commences to appear in the solution. The product is a pale-yellow, amorphous powder.

III. *Synthesis of Pyrone and of Chelidonic Acid.*—*Ethyl pyronetetracarboxylate* is formed when ethyloxalic chloride, COCl·COOEt (2 mols.), is added to a benzene solution of the sodium derivative of ethyl acetonedicarboxylate just described. When the reaction moderates, the mixture is heated in a reflux apparatus, shaken with water rendered slightly alkaline, and the uppermost layer of liquid dried and freed from the solvent. The product is a deep-yellow oil, which, after a time, deposits minute, acicular crystals of ethyl pyronetetracarboxylate; this melts at 94°, and dissolves readily in alcohol, benzene, acetic acid, and chloroform, but only sparingly in boiling water. It also dissolves in cold alkalis, forming yellow solutions.

Ethyl pyridonetetracarboxylate, $C_{17}H_{21}O_9N$, prepared by treating the preceding compound with warm, dilute ammonia, crystallises from alcohol in slender, colourless needles, melts at 229°, and dissolves very sparingly in cold water. It is a feeble base, and dissolves in cold, concentrated acids, but is reprecipitated from its solutions on the addition of much water.

When ethyl pyronetetracarboxylate is dissolved in boiling sulphuric acid (1 : 2), the liquid soon turns yellow, and a brisk evolution of carbonic oxide and anhydride takes place, probably owing to a radical decomposition of the compound.

Chelidonic Acid.—Ethyl pyronetetracarboxylate (3 grams) is heated with dilute (1 : 3 by weight) sulphuric acid (100 c.c.), the mixture strongly agitated until solution is complete, then immediately cooled, allowed to remain for 24 hours, and filtered; the solution is now neutralised with barium carbonate, the deposit washed by decantation with cold water, and then thoroughly extracted with boiling water. The extract, on concentration on the water-bath, deposits a small quantity of the sparingly soluble barium chelidonate, and from this the pure acid may be obtained, by converting it into the silver salt and saponifying. The acid may also be prepared by heating ethyl pyronetetracarboxylate with water (20 parts) and 1 or 2 drops of sulphuric acid for 6—8 hours at 120—130°, and proceeding as before. The yield is 8 per cent. The product has the same properties as the naturally occurring acid. It crystallises in interlaced, colourless needles containing 1 mol. H_2O, which it loses at 110—120°, in a vacuum over sulphuric acid, forms colourless solutions with alkaline carbonates, and yellow ones with the hydroxides; the latter, after boiling for some time, evolve an odour of acetone; it dissolves in boiling water, and very sparingly in the cold. The *silver* salt crystallises in long, colourless needles, sparingly soluble in boiling water. The anhydrous acid melts at 230—235° with evolution of carbonic anhydride. It dissolves in concentrated ammonia, and the solution yields ammonio-chelidonic acid, $C_7H_5O_5N$. The latter yields a dibromo-derivative, $C_7H_3O_5NBr_2 + 2H_2O$, crystallising in colourless needles. Both these compounds give the characteristic reactions of the corresponding derivatives obtained by Lieben and Haitinger (Abstr., 1885, 47, 965) from 2 : 6-pyronedicarboxylic acid.

Pyrone.—Ethyl pyronetetracarboxylate (6 grams) is dissolved in hot, dilute sulphuric acid (1 : 3), and the solution heated until a slight yellow coloration, accompanied by an incipient evolution of gas, becomes apparent. The solution is then neutralised with barium carbonate, the cold solution filtered, concentrated, and supersaturated with perfectly neutral calcium chloride. The pasty mass is shaken 8 or 10 times with ether; the ethereal solution, on drying, leaves a residue of pyrone in small, colourless crystals, which melt at 30°, and dissolve very readily in water. By treatment with concentrated ammonia it is converted into the pyridone, melting at 147°, identical with that obtained from ammonio-chelidonic acid, and yielding the same dibromo-derivative, $C_5H_3Br_2ON$, as described by Lieben and Haitinger (*loc. cit.*, and Abstr., 1884, 1196; compare this vol., p. 458).

S. B. A. A.

New Derivatives of Stearic Acid. By C. HELL and J. SADOMSKY (*Ber.*, **24**, 2388—2396).—The stearic acid employed was prepared from bassia oil, which is expressed from the seeds of *Bassia latifolia*, a tree growing in the Himalayas; the oil also contains palmitic and oleïc acids.

To obtain pure stearic acid, the oil is saponified with dilute sodium hydroxide, and after precipitating the soap with common salt, it is pressed and dissolved in water; dilute sulphuric acid is now added, and the precipitated fatty acids are repeatedly washed, by fusing under water, until the washings are neutral. The oleïc acid is then removed by triturating with cold alcohol, and the residue submitted to fractional distillation under diminished pressure, first at 100 mm., and afterwards at 15 mm.; after three fractionations, the portion passing over between 270° and 290° at 15 mm. is collected separately; it now contains 80 per cent. of stearic acid, and melts at 65°. It is dissolved in an excess of hot alcohol, and on the addition of alcoholic ammonia and a hot alcoholic solution of magnesium acetate, magnesium stearate separates; this is filtered off while hot, washed with hot alcohol, and, after repeating the operation, dried and decomposed with sulphuric acid (Heintz' method). The acid thus obtained is pure; it crystallises from alcohol in iridescent needles and plates, and melts at 69·2°.

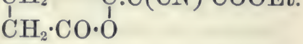
α-Bromostearic acid, $C_{18}H_{35}BrO_2$, is prepared by heating stearic acid (100 grams), well mixed with amorphous phosphorus (washed free from acid with water, and dried at 100°; 4·5 grams) in a reflux apparatus, and gradually dropping in bromine (dried by shaking with concentrated sulphuric acid; 36 c.c.). The reaction proceeds violently at first, but soon subsides; the heating is continued until bromine vapour is no longer perceptible. The reddish-brown melt is slowly poured into cold water, and washed by decantation until free from acid. It unites with water, forming an opaque mass resembling butter, the quantity taken up being dependent on the temperature; to remove this water it is heated with light petroleum, which dissolves the acid, forming a solution which floats on the water; the solution is separated and put aside, when crystals slowly make their appearance; after two or three recrystallisations, it is obtained as colourless, lustrous needles, or four-sided tables, and melts at 60°. It is insoluble in water, but dissolves readily in the ordinary organic solvents; it has not any irritating action on the skin. The *ethyl salt* is obtained when the acid is gently heated in alcoholic solution and a stream of hydrogen chloride passed through it, the compound separating as an oil; this solidifies on cooling, and after repeated crystallisation from alcohol, forms white, nodular aggregates, melts at 35—36°, and is readily soluble in the ordinary solvents.

α-Hydroxystearic acid, $C_{18}H_{36}O_3$, is formed when the brominated derivative is heated in a reflux apparatus with an excess of alcoholic soda for 24 hours; the sodium salt is collected, washed with alcohol and water, and decomposed with sulphuric acid; the free acid is dissolved in water, and the solution extracted with ether. It separates from a mixture of benzene (1 part) and light petroleum (3 parts) as a white, crystalline powder, melts at 84—85°, resolidifies at 71—70°, and is soluble in the ordinary solvents; 100 parts of alcohol dissolve 0·58 part at 20°. The *silver salt* is a white precipitate, which darkens on exposure to light; the *copper salt* is a green precipitate, whilst the *barium*, *lead*, and *cadmium salts* are white precipitates. The acid is not identical with that described by Fremy, and later by Saytzeff; it differs from this in its solidifying point and in solubility. The constitution of the bromo- and of the hydroxy-stearic acid is proved by the fact that the cyano-acid obtained from the former yields hexadecylmalonic acid on hydrolysis.

α-Amidostearic acid, $C_{18}H_{37}NO_2$, is obtained when the bromo-acid is heated in a sealed tube with an excess of alcoholic ammonia at 135—140° for 7—8 hours. The crystalline mass is heated on the water-bath to free it from ammonia and alcohol, and washed successively with boiling water, hot alcohol, ether, and dilute sodium hydroxide; it is then crystallised from boiling glacial acetic acid, when it forms a white, crystalline powder which melts at 221—222°; it is insoluble in alcohol, ether, and benzene.

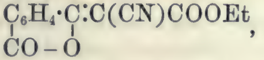
α-Anilidostearic acid, $C_{24}H_{41},NO_2$, is formed when the bromo-acid is heated with an excess of aniline in an oil-bath at 180—185°. The dark, reddish-brown, partially resinified mass is treated with dilute hydrochloric acid to remove the aniline, and washed with water and a little alcohol; it is then purified by repeated fractional precipitation from its solution in boiling glacial acetic acid, and final crystallisation from alcohol. It forms a white, granular powder, melts at 84·5°, and is readily soluble in benzene, ether, and alcohol, but only sparingly in light petroleum. A. R. L.

Action of Bibasic Acid Chlorides on Ethyl Sodiocyanacetate. By P. T. Muller (*Compt. rend.*, **112**, 1139—1141).—Succinic chloride (1 mol.) and ethyl sodiocyanacetate (2 mols.) react in presence of dry ether, yielding *ethyl succinocyanacetate*, a white compound soluble in chloroform in the cold. After crystallisation from chloroform, it melts at 125—126°. It has the composition



$$\begin{array}{l}\mathrm{CH_2\text{——}C{:}C(CN)\cdot COOEt.}\\ \mathrm{\;|\qquad\qquad\;|}\\ \mathrm{CH_2\cdot CO\cdot O}\end{array}$$

Phthalic chloride yields *ethyl phthalocyanacetate*,



$$\begin{array}{l}\mathrm{C_6H_4\cdot C{:}C(CN)COOEt}\\ \mathrm{\;|\qquad\;|}\\ \mathrm{CO-O}\end{array},$$

a product insoluble in ether and in water, but soluble in benzene or chloroform, from which it separates in white crystals melting at 175°, with decomposition. When these compounds are boiled with water, they yield ethyl cyanacetate and succinic acid or phthalic acid respectively. Prolonged ebullition with water splits up the ethyl cyanacetate into carbonic anhydride and ammonium acetate, probably with intermediate formation of acetonitrile.

The products obtained from the bibasic acid chlorides do not react with water in the same way as the products obtained by Haller from the monobasic acid chlorides. C. H. B.

Levulinic Acid: Acetonediacetic Acid Dilactone. By A. Michael (*J. pr. Chem.* [2], **44**, 113—129).—According to Kent and Tollens (*Annalen*, **227**, 229), levulinic acid distils in a vacuum at 157—160°; but the acid prepared by the author distilled at 148—149° at 15 mm.

Ethyl levulinate was prepared in three different ways, namely, by the action of hydrogen chloride on the acid dissolved in alcohol (Abstr., 1881, 410), by heating silver levulinate with ethyl iodide in a sealed tube at 100° for 15 hours, and by heating levulinic acid with alcohol and sulphuric acid; in each case the ethyl salt obtained was an oil, soluble in water, and boiling at 203—204° (compare *loc. cit.*, and Conrad, who prepared the salt by the last-mentioned method, and states that it is insoluble in water; Abstr., 1878, 137).

Ethyl levulinate hydrazone was obtained by Fischer's method, namely, the action of phenylhydrazine on the ethereal salt (Abstr., 1887, 149); it crystallises in plates or prisms, begins to soften at 103°, and melts at 106—108° (not 110°). Water is separated during its formation, not alcohol. Fischer (*loc. cit.*) has pointed out that α-ketonic acids will form hydrazones in the presence of mineral acids;

and although ethyl levulinate behaves as an α-ketonic acid derivative in this respect, levulinic acid does not, no hydrazone being formed.

The *oxime* $C_7O_3H_{13}N$, obtained by the action of hydroxylamine on ethyl levulinate, crystallises from light petroleum in large, colourless, obliquely truncated, prismatic needles, melts at 38—39°, and is sparingly soluble. This compound should be identical with that obtained by Müller (Abstr., 1883, 1129) by the action of ethyl iodide on silver γ-isonitrosovalerate, but Müller's ethyl derivative is an oil which does not solidify; the author repeated Müller's experiment, and obtained an oil half of which distilled between 135° and 160° under a pressure of 40 mm., and the other half between 160° and 164°. An analysis of the latter half led the author to conclude that it contained the crystalline oxime, but was too impure to crystallise.

The *oxime* $C_7H_{10}N_2O_4$, obtained by the action of hydroxylamine on acetonediacetic acid dilactone (Abstr., 1890, 30), crystallises with 2 mols. H_2O in large, lustrous, colourless, pointed prisms; it blackens at 240°, decomposes at 248—250°, and dissolves sparingly in cold, more easily in hot, water and alcohol. The aqueous solution is feebly acid, but does not evolve carbonic anhydride from sodium carbonate.

Bredt's hydrazone (Abstr., 1890, 864) is also obtained when the dilactone reacts with phenylhydrazine hydrochloride in aqueous solution; it begins to melt at 290°, and melts completely at 298—301°, with discoloration. When the dilactone and phenylhydrazine hydrochloride react in presence of sodium acetate, a compound which crystallises in prismatic plates is formed; this softens at 130—135°, solidifies again at a higher temperature, and decomposes at about 230°.

The author discusses the probable constitution of ethyl levulinate and acetonediacetic acid dilactone dioxime in the light of the above reactions, and concludes his paper by a seriatim refutation of Bredt's reasons for considering levulinic acid to be a γ_2-hydroxylactone (*Annalen*, **253**, 314; **256**, 314; Abstr., 1890, 863). Our present knowledge of the subject is in favour of the ketonic constitution for levulinic acid. A. G. B.

Action of Zinc on Ethyl Dibromosuccinate. By A. Claus (*J. pr. Chem.* [2], **44**, 110—112).—A reply to Michael and Schulthess (this vol., p. 1184) on the question as to whether an intermediate compound of zinc with the elements of ethyl dibromosuccinate is formed prior to the decomposition into zinc bromide and ethyl fumarate. W. P. W.

Conversion of Maleïc Acid into Fumaric Acid. By Z. H. Skraup (*Monatsh.*, **12**, 107—145; compare Abstr., 1890, 1397).—At a temperature of 100°, and under the ordinary pressure, water does not convert maleïc into fumaric acid; but at a higher temperature, and under increased pressure, the change takes place, the amount of fumaric acid produced varying considerably with the conditions, although in no case is the conversion complete (compare Tanatar, *Chem. Centr.*, 1891, 17). At low temperatures, part of the maleïc acid remains unchanged, whilst at higher temperatures it is to a large extent converted into a malic acid, which is most probably identical with the inactive variety obtained by Loydl from fumaric acid and sodium hydroxide solution. The same inactive variety of malic acid is obtained on heating an aqueous solution of fumaric acid at 180—190°.

Concentrated hydrochloric acid converts maleïc acid at ordinary temperatures into a mixture of fumaric acid and chlorosuccinic acid, but the latter is not formed by the action of hydrochloric acid on fumaric acid. Hydriodic acid rapidly converts maleïc into fumaric acid, probably with the production of some succinic acid. Benzenesulphonic acid, like sulphuric acid, is almost without action on maleïc acid under ordinary conditions; whilst oxalic acid at a high temperature induces conversion into malic acid, the oxalic acid itself undergoing decomposition, with formation of formic acid and carbonic anhydride. Heated in sealed tubes with benzenesulphonic acid, or with sulphuric acid, maleïc acid in aqueous solution is only very slowly converted into fumaric acid, the presence of these acids appearing to hinder the change. Organic acids, such as formic, acetic, butyric, and isobutyric, have very little influence on the conversion of maleïc acid.

The copper, lead, and silver salts of maleïc acid are partly converted into fumaric acid on treatment with hydrogen sulphide, the copper and lead salts giving the largest yields. Hydrogen sulphide alone has little effect on maleïc acid, but when an aqueous solution of the acid is saturated with hydrogen sulphide and sulphurous anhydride and then warmed, a very considerable yield of fumaric acid is obtained.

The author gives numerous details of his work, and in conclusion supports the view that the conversion of maleïc into fumaric acid is a purely catalytic action, and is quite independent of the presence or absence of water during the change (compare Anschütz, Abstr., 1890, 363). G. T. M.

Methylene Derivatives of Carbamide and of Thiocarbamide. By F. v. Hemmelmayr (*Monatsh.*, **12**, 89—97).—*Methylenethiocarbamide*, $\mathrm{CS}{<}\substack{\mathrm{NH}\\ \mathrm{NH}}{>}\mathrm{CH_2}$, or, according to the investigations of Storch, $\mathrm{NH{:}C}{<}\substack{\mathrm{S}—\\ \mathrm{NH}}{>}\mathrm{CH_2}$, is obtained on mixing together equal weights of thiocarbamide and the so-called chloromethyl alcohol of Lösekann (*Chem. Zeit.*, **14**, 1408—1409). Much heat is developed during the reaction, and hydrogen chloride escapes. The product, which solidifies on cooling, is freed from methyl alcohol, dissolved in water, and the solution gently warmed, when the compound is precipitated in the form of white, insoluble flocks. It is almost insoluble in all ordinary solvents, 1 part requiring 50,000 parts of water and 8,000 of alcohol for its solution at ordinary temperatures. When warmed with mineral acids and with bases, it dissolves, forming thiocarbamide and formaldehyde. Nitric acid, potassium permanganate, and bromine water oxidise the sulphur of the compound to sulphuric acid. On long-continued boiling with water, methylenethiocarbamide is resolved into thiocarbamide and formaldehyde. It commences to decompose at 180° with evolution of ammonia, and at 200° melts, forming a brown liquid; in its chemical and physical properties it closely resembles ethylidenethiocarbamide (compare Reynolds, *Krit. Zeitschr.*, 1871, 325).

Methylenecarbamide, $CO<^{NH}_{NH}>CH_2$, is prepared by warming a mixture of equal weights of carbamide and chloromethyl alcohol, and treating the product in a manner similar to that indicated in the preparation of the corresponding thiocarbamide, to which the new compound shows a considerable resemblance, both in appearance and properties. It begins to decompose at 200°, with evolution of ammonia, and at 240° melts to a brown liquid, which solidifies on cooling, and is soluble in hot water. Mineral acids resolve it into carbamide and formaldehyde, and the same change is produced by long-continued boiling with water. G. T. M.

Formation of Uric Acid and of Xanthine Bases, and the Production of Leucocytosis in Mammals. By J. HORBACZEWSKI (*Monatsh.*, **12**, 221—275).—It has been previously shown (Abstr., 1890, 184) that uric acid is produced when an extract of the spleen is warmed for some hours with fresh arterial blood or with a dilute solution of hydrogen dioxide, or exposed to the air at a moderate temperature. The extract used in the experiments was prepared by digesting the fresh spleen with distilled water at 50° for eight hours; during this process putrefaction sets in, and a moderate gas evolution commences. The filtered extract is then carefully precipitated with lead acetate, allowed to settle, and the clear solution filtered. The extract obtained in this way contains substances which are decomposed on boiling in absence of oxygen with formation of xanthine and hypoxanthine; if, however, decomposition takes place in presence of oxygen, a quantity of uric acid, equivalent to that of the xanthine bases, is produced. Experiments showed that these mother substances are present in the lymphatic elements of the spleen, especially in the nuclei, as has been suggested previously by Kossel, Schröder, and others.

An examination of a number of organs, obtained chiefly from young calves, but in some cases from fresh corpses, showed that they all, except the sinews, give uric acid when treated with fresh blood until putrefaction sets in; with the exception of calves' brain and calves' lungs, which in one case each gave moderately large quantities of uric acid, neither the blood nor any of the organs contains any appreciable quantity of this acid before the treatment.

When a dilute alkaline solution of nucleïn, prepared from the spleen as described by Miescher, is injected subcutaneously into a rabbit, the quantity of uric acid in the urine is increased; the same result is observed when nucleïn, suspended in water, is introduced into the human system.

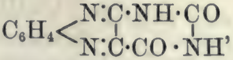
The increase in the number of leucocytes in the blood of man, on taking mixed animal and vegetable food after a fast of 18 hours, is accompanied by an increased secretion of uric acid, but the total quantity of nitrogen excreted in the urine is not very materially augmented. When vegetable food only is taken after a fast of 18 hours, the results vary greatly with different individuals; in some cases the quantity of uric acid excreted is doubled, in others a hardly perceptible increase takes place.

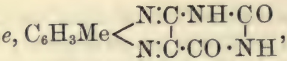
Various experiments showed the close relationship between the number of leucocytes in the blood and the quantity of uric acid secreted in the urine; it seems probable that in mammals, under normal conditions, the uric acid is formed from the decomposition products of the leucocytes.

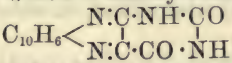
Quinine and atropine, given in small doses to man after an 18 hours fast, cause a diminution in the number of leucocytes in the blood, and also lessen the secretion of uric acid; small doses of pilocarpin, given under the same conditions, increase the number of leucocytes, and in some cases the quantity of uric acid secreted is also increased; antipyrine and antifebrine increase the number of leucocytes, but diminish the uric acid secretion.

Nucleïn from spleen, and probably also other nucleïns, produce, compared with albumin, a relatively very intense leucocytosis; in the case of a man who had fasted for 18 hours, a dose of 5 grams of nucleïn increased the number of leucocytes 83 per cent.; in two other experiments with different individuals the increase was 53·1 and 60·5 per cent. respectively. This result is probably due to a proliferation of the lymphoid elements in the lymphoid tissues of the intestinal canal and mesenterial and lymphatic glands, as well as in the spleen, marrow, &c. F. S. K.

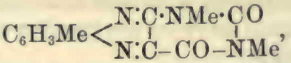
Azines of the Uric Acid Group. By O. KÜHLING (*Ber.*, **24**, 2363—2369).—Hinsberg (Abstr., 1885, 909) obtained hydroxycarboxytoluquinoxaline ureïde by mixing aqueous solutions of 3 : 4-diamidotoluene and alloxan; the author has succeeded in preparing alloxazine and certain of its derivatives by employing the hydrochloride of the orthodiamine instead of the free base, under the conditions described below.

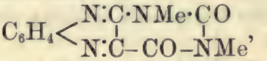
Alloxazine,  $C_6H_4<\begin{matrix}N{:}C\cdot NH\cdot CO\\ | \qquad\quad |\\ N{:}C\cdot CO\cdot NH\end{matrix}$, is formed when aqueous or alcoholic solutions containing equivalent quantities of alloxan and 1 : 2-diamidobenzene hydrochloride are mixed and heated for a short time; the liquid becomes yellow, and a thick, yellow precipitate separates, which is collected and repeatedly boiled with water; it consists of microscopic needles. The compound is insoluble in water and in ether and very sparingly soluble in alcohol; it dissolves in alkali carbonates and is reprecipitated on the addition of a mineral acid; it decomposes above 300°. The alkali salts are readily soluble in water and are partially decomposed by carbonic acid; the *barium salt* is a flocculent precipitate which could not be obtained of constant composition. The *azine* is not completely converted into the corresponding hydroxyquinoxalinecarboxylic acid when heated with an excess of aqueous potassium hydroxide for nine hours, thus differing from Hinsberg's ureïde (*loc. cit.*).

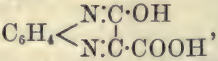
Tolualloxazine,  $C_6H_3Me<\begin{array}{l}N{:}C{\cdot}NH{\cdot}CO\\ \quad\;|\qquad\qquad\;\;|\\ N{:}C{\cdot}CO{\cdot}NH\end{array}$, is obtained from alloxan and 3 : 4-diamidotoluene hydrochloride in a similar manner to the last-described compound, which it closely resembles.

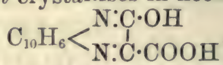
Naphthalloxazine,  $C_{10}H_6<\begin{array}{l}N{:}C{\cdot}NH{\cdot}CO\\ \quad\;|\qquad\qquad\;\;|\\ N{:}C{\cdot}CO{\cdot}NH\end{array}$, is produced from alloxan and 1 : 2-diamidonaphthalene hydrochloride. It forms a yellow, microscopic powder, decomposes above 300°, does not dissolve in alkali carbonates, but is readily soluble in caustic alkalis; it is very sparingly soluble in water and only slightly more so in alcohol; the *barium salt* is a yellow precipitate, insoluble in water, and decomposes when dried in the desiccator.

When hot aqueous solutions of alloxantin and 3 : 4-diamidotoluene hydrochloride are mixed, tolualloxazine, identical with that described above, is formed.

Dimethyltolualloxazine,  $C_6H_3Me<\begin{array}{l}N{:}C{\cdot}NMe{\cdot}CO\\ \quad\;|\qquad\qquad\quad\;|\\ N{:}C-CO-NMe\end{array}$, is obtained when an excess of aqueous 3 : 4-diamidotoluene hydrochloride is added to a boiling aqueous solution of tetramethylalloxantin and the mixture boiled for a time. It does not show acidic properties; it crystallises from boiling water, in which it is sparingly soluble (0·5 gram requires for dissolution 2 litres of boiling water), in delicate, yellowish-white needles, but is best crystallised from boiling alcohol, which dissolves it more readily. It melts at 205—210°.

Dimethylalloxazine,  $C_6H_4<\begin{array}{l}N{:}C{\cdot}NMe{\cdot}CO\\ \quad\;|\qquad\qquad\quad\;|\\ N{:}C-CO-NMe\end{array}$, is a yellowish-white, sandy, crystalline powder; it is very sparingly soluble in water, more readily in boiling alcohol, and melts at 236°.

Hydroxyquinoxalinecarboxylic acid,  $C_6H_4<\begin{array}{l}N{:}C{\cdot}OH\\ \quad\;|\\ N{:}C{\cdot}COOH\end{array}$, is formed when aqueous solutions of 1 : 2-diamidobenzene and mesoxalic acid are heated; it separates from boiling water in delicate, yellow needles and decomposes at 200°; the *barium salt* crystallises in needles.

Naphthazinehydroxycarboxylic acid,  $C_{10}H_6<\begin{array}{l}N{:}C{\cdot}OH\\ \quad\;|\\ N{:}C{\cdot}COOH\end{array}$, is only sparingly soluble in boiling water; the *barium salt* is a yellowish, flocculent precipitate.

Toluquinoxalinecarboxylic acid, prepared from 3 : 4-diamidotoluene and mesoxalic acid, is identical with that described by Hinsberg (*loc. cit.*).

A. R. L.

Thiophen. By G. Minunni (*Gazzetta*, **21**, 143—148).—When thiophen, prepared by Volhard and Erdmann's method, is heated with an equal weight of phenylhydrazine, evolution of hydrogen sulphide commences after a few minutes and continues for some hours, but on distilling the product nothing but unaltered thiophen and phenylhydrazine are obtained. Similar results are obtained on operating in a closed tube at 220°.

When the thiophen recovered from the above operations is heated at 200—210° in a closed tube with litharge, no change is observed, but when thiophen which has not been treated with phenylhydrazine is heated with litharge, lead sulphate is formed. From this it is evident that the evolution of hydrogen sulphide is due to the presence of some impurity in the thiophen.

If 1 part of phenylhydrazine be gradually dropped into 10 parts of the impure thiophen, a white, crystalline substance, soluble in excess of the base, is precipitated; this compound is not formed if thiophen which has been already heated with phenylhydrazine is employed. The crystalline compound thus formed is identical with the phenylhydrazine phenylthiocarbazide prepared by E. Fischer (*Annalen*, **190**, 114) by the action of phenylhydrazine on carbon bisulphide. The impurity is therefore carbon bisulphide. Rectified thiophen contains an average of about 0·2 per cent. of this substance, and unrectified thiophen a much larger quantity.

The author records a very characteristic property of phenylhydrazine phenylthiocarbazide; on passing a current of dry oxygen through its solution in carbon bisulphide, hydrogen sulphide is evolved and diphenylthiocarbazide deposited as a white, crystalline powder.

E. v. Meyer (Abstr., 1886, 349) states that a mixture of phenylhydrazine and benzene deposits a crystalline compound containing sulphur and melting at 96°; he considers its formation to be due to an impurity in the phenylhydrazine employed. This substance agrees in all its recorded properties with phenylhydrazine phenylthiocarbazide, and is most probably derived from carbon bisulphide in the benzene employed, as commercial benzene always contains this impurity. W. J. P.

Note.—A short time before the publication of this paper, Liebermann and Seyewitz (this vol., p. 684) stated that the carbon bisulphide in commercial benzene could be estimated by means of its reaction with phenylhydrazine. W. J. P.

Ring and Nucleus Structure of Aromatic Hydrocarbons. By W. Vaubel (*J. pr. Chem.* [2], **44**, 137—149).—The author reviews the structural formulæ hitherto proposed for benzene, and regards Loschmidt's (*Monatsh.*, **11**, 28; Abstr., 1890, 602) as the least objectionable of them. But even this does not express his ideas of the benzene molecule, for the summits of the tetrahedra are all in the same plane, a dissymmetry that is not warranted by the behaviour of benzene. None of the formulæ hitherto suggested complies with the fact that ortho- and para-derivatives are chiefly formed (1) when benzene and toluene are chlorinated and brominated; (2) when halogen substitution products of the methyl group in toluene are nitrated; (3) when chloro-, bromo-, and iodo-benzene are nitrated; (4) when acetanilide is nitrated, producing ortho- and para-nitraniline; (5) when phenol is nitrated, chlorinated, and sulphated; (6) when cinnamic and hydrocinnamic acids are nitrated. Nor does any of them comply with the facts that meta-derivatives are chiefly formed (1) when benzaldehyde, acetophenone, benzoic acid, and phenyl cyanide are nitrated; (2) when benzene is heated with fuming sulphuric acid at 200°, the metasulphonic acid at first formed being converted into the para-acid by longer heating.

The author's formula for benzene is a symmetrical arrangement of Loschmidt's formula, that is to say, instead of the summits of the six tetrahedra being all on the same side of the central plane, three of them are on each side. He explains away various difficulties by aid of this formula and develops it for naphthalene, in which case it complies with Bamberger's qualifications (*Annalen*, **257**, 1; Abstr., 1890, 1299), and for anthracene. A. G. B.

Constitution of Cymene. By M. Fileti (*J. pr. Chem.* [2], **44**, 150—152).—The author has repeated Widman's experiments (this vol., p. 986), and fully confirms his conclusion that cymene is an isopropyl derivative. A. G. B.

Metacyanobenzyl Chloride and Metacyanobenzaldehyde. By P. Reinglass (*Ber.*, **24**, 2416—2424).—Metacyanobenzyl chloride, $CN\cdot C_6H_4\cdot CH_2Cl$, is obtained by treating metacyanotoluene with chlorine at 150° until it has gained 30 per cent. in weight, spreading on a tile the reddish-yellow, crystalline cake which forms on cooling, and then dissolving it in a small quantity of boiling alcohol. It separates from alcohol in small, white plates or colourless prisms, and from boiling water in long, delicate needles, melts at 67°, boils at 258—260° (760 mm.). It is also soluble in ether, chloroform, and benzene, and is slightly volatile with aqueous vapour. Its vapour has a strong action on the eyes and mucous membrane of the nose; whilst the substance itself produces an irritation on the skin, and a burning on the tongue.

Metacyanobenzal chloride, $CN\cdot C_6H_4\cdot CHCl_2$, is formed by treating metacyanotoluene with chlorine until it has gained 60 per cent. in weight; when the red product is distilled, it passes over with the evolution of hydrogen chloride between 272° and 275° (765 mm.) as a clear, yellow liquid.

Paracyanobenzal chloride, $CN\cdot C_6H_4\cdot CHCl_2$, is prepared by treating paracyanobenzyl chloride (Mellinghoff, Abstr., 1890, 239) with chlorine until it has gained 30 per cent. in weight; it is a colourless liquid boiling at 273—276° (770 mm.).

Metacyanobenzyl cyanide, $CN\cdot C_6H_4\cdot CH_2\cdot CN$, is obtained by dissolving metacyanobenzyl chloride (6 grams) and potassium cyanide (3 grams) in water (25 c.c.) and alcohol (60 c.c.), heating the mixture on the water-bath for $\frac{3}{4}$ hour, distilling off two-thirds of the alcohol, and pouring the residue into water; the precipitated compound is crystallised from hot water; it forms delicate needles, melts at 84°, and is easily soluble in alcohol, ether, chloroform, and benzene.

ω-Chlorometatoluamide, $CONH_2\cdot C_6H_4\cdot CH_2Cl$, is formed by dissolving metacyanobenzyl chloride in five times its weight of concentrated sulphuric acid and allowing it to remain for 15 hours (compare Gabriel, Abstr., 1887, 1038; Mellinghoff, *loc. cit.*), then pouring it into eight times its volume of water, neutralising with dilute ammonia, and crystallising the precipitated compound from a small quantity of hot alcohol. It melts at 124°, and is very readily soluble in alcohol, ether, and hot water. Its dust causes sneezing.

ω-Chlorometatoluic acid, $COOH\cdot C_6H_4\cdot CH_2Cl$, is produced by heating metacyanobenzyl chloride with 20 times its weight of concentrated hydrochloric acid in a reflux apparatus, when the acid separates from the solution on cooling in small, delicate needles. To purify it, it is dissolved in dilute ammonia, filtered, and reprecipitated by the addition of hydrochloric acid. When recrystallised from hot water, it melts at 135°, and is readily soluble in alcohol and ether. The *copper salt* separates as a sparingly soluble, bright blue precipitate on adding copper sulphate to an aqueous solution of the ammonium salt.

Metacyanobenzylphthalimide, $CN\cdot C_6H_4\cdot CH_2.N\colon C_8H_4O_2$, is prepared by heating an intimate mixture of dry metacyanobenzyl chloride (7 grams) and potassium phthalimide (9 grams) in a globular flask at 125—130° for 3—4 hours; when cold, the product is boiled with water and the solution filtered while hot; the granular powder which separates from the filtrate is purified by crystallising it from glacial acetic acid; it melts at 147°.

ω-Amidometatoluic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot NH_2$, is obtained by heating the last-described imide (2 grams) with concentrated hydrochloric acid (10 c.c.) at 200° for 3 hours in a sealed tube, diluting the product with a little water, filtering off the phthalic acid, and isolating the new acid from the filtrate by means of its mercuric salt, which is sparingly soluble in water; this is decomposed by a current of hydrogen sulphide, sodium acetate added to the filtrate, and the liquid slowly evaporated, when the acid separates in small, white scales which melt at 215—218°. An intermediate compound, *metacarboxybenzylphthalamic acid*, $COOH\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot COOH$, is formed by heating the phthalimide (5 grams) with 30 per cent. sodium hydroxide (40 c.c.) for 20—25 minutes, shaking frequently, and then adding water and an excess of hydrochloric acid, when it is precipitated; when recrystallised from hot alcohol, it melts at 228—230° (compare Günther, Abstr., 1890, 977). If this compound is heated with concentrated hydrochloric acid at 200° in a sealed tube for 3 hours, ω-amidometatoluic acid is formed. The *platinochloride*, $(C_8H_9NO_2)_2,H_2PtCl_6$, is a yellow ochreous precipitate, and the *aurochloride* forms yellow prisms and melts at 175—177° with decomposition.

Dimetacarboxybenzyl ether, $O(CH_2\cdot C_6H_4\cdot COOH)_2$, is obtained by heating metacyanobenzyl chloride (5 grams) with 33 per cent. potassium hydroxide in a reflux apparatus for 3 hours, diluting with water, and, after precipitating the filtrate with an excess of hydrochloric acid, crystallising from hot water; it melts at 180°, and is sparingly soluble in ether, chloroform, and benzene.

Metacyanobenzaldehyde, $CN\cdot C_6H_4\cdot COH$, is produced by adding metacyanobenzyl chloride (8 grams) to a hot solution of copper nitrate (16 grams) in water (160 c.c.) and boiling for 16—17 hours, when an intensely green solution is obtained; on cooling, this deposits white needles, which are dissolved in ether, and the ethereal solution mixed with an aqueous solution of sodium hydrogen sulphite; the additive compound is collected, washed with ether and alcohol, and steam distilled in the presence of an alkali; the distillate is extracted with ether, which leaves long needles on evaporation. It melts at 79—81°, yields a metallic mirror with ammoniacal silver nitrate, and gives all the reactions of an aldehyde. The *hydrazone*, $CN\cdot C_6H_4\cdot CH\colon N_2HPh$, crystallises from alcohol in small, yellow needles, and melts at 120°; the *oxime*, $CN\cdot C_6H_4\cdot CH{:}NOH$, melts at 99—101°, and yields metadicyanobenzene (m. p. 157°) on treatment with acetic anhydride.

Paracyanobenzaldehyde, $CN\cdot C_6H_4\cdot COH$, is obtained from paracyanobenzyl chloride; it crystallises from hot water in long, white needles, melts at 96—98°, is volatile with steam, and is readily soluble in alcohol, ether, and chloroform. The *hydrazone* melts at 135—137°, and the *oxime* at 145°.

Both the last-described aldehydes may be prepared more quickly and a better yield obtained by boiling the corresponding benzal chlorides with silver nitrate.

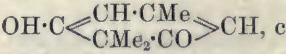
Paraldehydobenzoic acid, $COOH\cdot C_6H_4\cdot COH$, is formed on heating paracyanobenzaldehyde with 25 times its weight of concentrated hydrochloric acid in a reflux apparatus; it crystallises in microscopic needles, commences to melt at 285°, and is soluble in water, but more so in alcohol and ether. The *copper salt* is a bright blue precipitate; the oxime melts at 208—210°, whilst the *hydrazone* melts at 212—214°.

Metaldehydobenzoic acid is obtained from metacyanobenzaldehyde in a similar manner to its isomeride; it melts at 164—166°; the *copper salt* is a greenish-blue precipitate; the *oxime* melts at 165° with decomposition, whilst the *hydrazone* melts at 112—115°. Orthaldehydobenzoic acid (phthalaldehydic acid) has been described by Racine (Abstr., 1886, 549). A. R. L.

Products of Condensation of Metanitrobenzaldehyde with Phenol and Resorcinol. By G. de Varda and M. Zenoni (*Gazzetta*, **21**, 174—183; compare this vol., p. 1378).—*Metanitrodioxytriphenylmethane*, $CH(C_6H_4\cdot OH)_2{:}C_6H_4\cdot NO_2$, is obtained by melting together a mixture of phenol and metanitrobenzaldehyde in theoretical proportion, slowly adding sulphuric acid ($H_2SO_4 + 2H_2O$), 1 mol., then gradually heating and keeping the mixture at 130°, until no further action is observed. The product is freed from unaltered phenol and metanitrobenzaldehyde by steam distillation, boiled with a large quantity of water, and the solution filtered and allowed to remain; on cooling, the condensation product is deposited. It is an amorphous, dark-yellow powder, melting at 59—60°, very little soluble in ether, chloroform, benzene, or light petroleum, and almost insoluble in carbon bisulphide, soluble in about 10,000 parts of boiling water. It is not volatile with steam, and is for the most part decomposed on distillation under diminished pressure.

Metanitrophenyldiresorcinolmethane, $CH[C_6H_3(OH)_2]_2\cdot C_6H_4\cdot NO_2$, is readily obtained without the aid of a condensing agent by heating the equivalent proportions of resorcinol and metanitrobenzaldehyde at 150°, and purifying the product by washing it with water and precipitation from its alcoholic and ethereal solutions. It is a yellowish, amorphous powder, slowly darkened by the action of air and light, and melts at 97—100°; it is soluble in ether, alcohol, and acetic acid, almost insoluble in light petroleum, benzene, chloroform, and carbon bisulphide; it is precipitated unaltered from its alkaline solution by acids. The substance cannot be distilled with steam, or under diminished pressure.

The precise constitutions of the above two compounds are unknown. W. J. P.

Methylation of Symmetrical Orcinol. By A. Kraus (*Monatsh.*, **12**, 191—204; compare Herzig and Zeisel, Abstr., 1890, 1405).—Anhydrous orcinol melts at 106·5—111° or on remelting after solidification at 108—111°; on warming with methyl iodide and potash in methyl alcoholic solution, and treatment of the product with potash, a dimethylorcinol is obtained on acidifying and extracting with ether; it has the formula $C_6HMe_3(OH)_2$ [OH = 2 : 3; Me_3 = 2 : 4 : 5] or  $\mathrm{OH{\cdot}C}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{\cdot}CMe}}{\mathrm{CMe_2{\cdot}CO}}{>}\mathrm{CH}$, crystallises from methyl alcohol, and melts at 204°. The *acetyl*, *benzoyl*, and *bromo*-derivatives are viscid liquids.

The portion of the original methylation product which is insoluble in potash, on distillation under reduced pressure, yields *dimethylorcinol dimethyl ether*, $C_6HMe_3(OMe)_2$; this crystallises from glacial acetic acid, and melts at 93—94°. The fraction boiling at 135—138° under a pressure of 18—22 mm. was treated with hydriodic acid, and the product formed, when purified, melted at 156°. This is a *dimethylorcinol* isomeric with the one above described, as it contains two hydroxyl groups. Since it is prepared from the dimethyl ether, it probably has the first of the two formulæ given above, whilst the compound melting at 204° is probably represented by the second. J. B. T.

Action of Light on Anethoïl. By G. de Varda (*Gazzetta*, **21**, 183—188).—Crystalline anethoïl, when exposed to sunlight, soon liquefies, and, on submitting it to distillation, a fraction boiling between 251° and 296° is obtained. This solidifies on cooling, and, when purified by repeated crystallisation from strong alcohol, is found to be a new polymeride of anethoïl, which the author terms *photoanethoïl.* The residue left in the retort, when crystallised from alcohol, yields the same substance.

Photoanethoïl forms minute, white, nacreous, tabular crystals, melts at 207°, and has neither taste nor odour. It is insoluble in water, sparingly soluble in ether, alcohol, light petroleum, chloroform, and boiling acetic acid, sublimes in microscopic plates, and does not volatilise with aqueous vapour. Its solution in chloroform has no rotatory action on polarised light. Anethoïl yields about 0·5 per cent. of photoanethoïl by the above treatment.

Metanitrophenyldianethoïlmethane, $NO_2{\cdot}C_6H_4{\cdot}CH[C_6H_3(C_3H_5){\cdot}OMe]_2$, is obtained when the theoretical proportions of anethoïl and metanitrobenzaldehyde are fused together with sulphuric acid (H_2SO_4 + H_2O) at 150°. The crude product is boiled out with water and treated with superheated steam; the residue is then extracted with ether, and the solution filtered and poured into alcohol; the precipitate thus formed is collected, again dissolved in ether, and reprecipitated by the addition of light petroleum. The pure substance is a yellow, amorphous powder without odour or taste, melts at 165—170°, is insoluble in alkalis and sulphuric acid, almost insoluble in alcohol, fairly soluble in chloroform, ether, carbon bisulphide, and acetic acid. It does not sublime on heating, and cannot be distilled in a current of steam.

When photoanethoïl is heated with metanitrobenzaldehyde and acid, the same condensation product is produced, showing that photoanethoïl is a true polymeride of anethoïl. W. J. P.

Constitution of Quinone. By J. U. Nef (*Amer. Chem. J.*, **13**, 422—428; compare Abstr., 1890, 1270).—In his previous paper (Abstr., 1890, 1270), the author pointed out that Fittig's formula must represent the constitution of quinone. It has been asserted, however, that the proof that quinone dibromide has its bromine atoms in the ortho-position is not absolute (compare Claus, this vol., p. 44; Nietzki, *ibid.*, 189; Kehrmann, *ibid.*, 432).

The analogy between the behaviour of quinone dibromide and tetrabromide towards zinc-dust and acetic acid (Abstr., 1890, 1272) and the behaviour of v. Baeyer's additive products of hydrogenated terephthalic acids (Abstr., 1888, 1069; 1889, 1176; *Annalen*, **258**, 11) is such that there can be little doubt that these compounds are of similar constitution.

Since no orthodibromoquinone is formed when hydrogen bromide is removed from quinone tetrabromide by boiling it with aqueous alcohol (Abstr., 1890, 1272), the hydrogen bromide must be split off from the ortho-position, and it is rendered highly probable that the addition of bromine takes place in ortho-positions; the existence of the following compounds furnishes absolutely conclusive proof that this is the case:—

Quinone dichloride [$O_2 : Cl_2 = 1 : 4 : 2 : 3$] is pale yellow, melts at 143°, and distils unchanged.

Quinone tetrachloride [$O_2 : Cl_4 = 1 : 4 : 2 : 3 : 5 : 6$] is colourless, sublimes without melting, and undecomposed.

Quinone dichloride dibromide [$O_2 : Cl_2 : Br_2 = 1 : 4 : 2 : 3 : 5 : 6$] is colourless, and melts at 195°.

The properties of these substances are similar to those of the two bromine additive products (Abstr., 1890, 1272), except that they are more stable. That the constitution of the dichloride dibromide is as given above, and not $O_2 : Cl_2 : Br_2 = 1 : 4 : 3 : 6 : 2 : 5$, is proved by the fact that, when boiled with alcohol and water, it yields about equal parts of *meta-* and *para-chlorobromoquinone* of the constitution $O_2 : Cl : Br = 1 : 4 : 6 : 2$ and $1 : 4 : 3 : 6$ respectively. The latter crystallises in plates which melt at 172°, the former in needles melting at 113°; they were easily separated by fractional crystallisation from ether, in which the para-compound is less soluble. The direct synthesis of these two substances in the following ways proves that their constitution is correctly given above.

(*a.*) Parachlorobromonitrobenzene [$NO_2 : Cl : Br = 1 : 2 : 5$] was reduced by zinc-dust and acetic acid to chlorobromaniline (m. p. 43°), which, on boiling with manganese dioxide and sulphuric acid, gave parachlorobromoquinone, identical with the above product and with Levy and Schultz's chlorobromoquinone (Abstr., 1882, 509).

(*b.*) Chloroparanitrophenol [$OH : Cl : NO_2 = 1 : 2 : 4$] was converted into bromochloroparanitrophenol [$OH : Cl : NO_2 : Br = 1 : 2 : 4 : 6$] (m. p. 138°) and then reduced with tin and hydrochloric acid. The chlorobromamidophenol thus produced was boiled with manganese dioxide and sulphuric acid, when metachlorobromoquinone, identical with the above, was obtained.

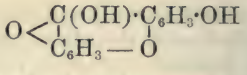
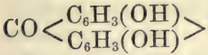
If quinone dichloride dibromide has its chlorine atoms in the para-position [2 : 5] and it be decomposed by aqueous alcohol, assuming the splitting off of halogen hydride to take place in great part from ortho-positions, the compound produced would be paradichloroquinone (m. p. 164°) since the chlorine atoms are more firmly bound than the bromine atoms. Paradibromoquinone (m. p. 188°) and metachlorobromoquinone are the other possible products. As a fact, however, neither paradichloro- nor paradibromo-quinone was formed.

If, however, the quinone dichloride dibromide have the constitution assigned to it above, and halogen hydride be split off from para-positions, only orthochlorobromoquinone and metachlorobromoquinone could be formed.

The addition of halogens to quinone is thus proved to take place in ortho-positions, and the splitting off of halogen hydride also to take place from ortho-positions—facts which are explicable by Fittig's formula for quinone, but will not uphold Claus' diagonal ketone formula.

The publication of experimental details is promised, and the author concludes with the observation that it seems probable to him that the conversion of quinol into quinone is accompanied by a rearrangement of the valencies of the carbon atoms forming the closed chain (Nietzki, *loc. cit.*), on the ground that neither quinolcarboxylic acid, tolylquinolcarboxylic acid, paradihydroxyterephthalic acid, nor the ethyl salts of these acids, can be oxidised to the corresponding quinones. A. G. B.

Euxanthone. By J. HERZIG (*Monatsh.*, **12**, 161—171).—The author has studied various derivatives of euxanthone with the object of showing its relationship to quercetin. Both these substances are yellow, but yield colourless acetyl derivatives which are readily hydrolysed by treatment with sulphuric acid.

Euxanthone ethyl ether, $C_{13}H_7O_3{\cdot}OEt$, crystallises from alcohol in long, yellow needles, and melts at 144—145°. It does not dissolve in potash, but yields an unstable, insoluble salt by the action of alcoholic potash; the latter resembles the corresponding quercetin derivative, and readily undergoes dissociation in presence of water. *Acetyl euxanthone ethyl ether*, $C_{13}H_6AcO_3{\cdot}OEt$, crystallises from alcohol in long, colourless, lustrous needles, and melts at 180—182°. The compound readily yields a euxanthone diethyl ether, $C_{13}H_6O_2(OEt)_2$, on treatment with potash and ethyl iodide. Euxanthone ethyl ether is formed from the diethyl derivative when the latter is heated with alcoholic potash in a sealed tube for four hours at 130—150°. An isomeric *monethyl ether* is obtained by treating the diethyl derivative with 20 parts of concentrated sulphuric acid for three hours at 100°; it crystallises from alcohol in colourless needles, melts at 223—225°, and is readily soluble in dilute potash. The constitution of this compound is being further investigated. The existence of two monethyl ethers makes it appear possible that euxanthone may exist in two forms, represented by the formulæ  $O<\begin{matrix}C(OH)\cdot C_6H_3\cdot OH\\ |\qquad\qquad\quad |\\ C_6H_3 - O\end{matrix}$ and  $CO<\begin{matrix}C_6H_3(OH)\\ C_6H_3(OH)\end{matrix}>O$, or it may be that the hydroxyl groups occupy different relative positions in the molecule. That there is considerable difference between euxanthone and quercetin is proved by the fact that, whilst the latter is readily decomposed by alkalis, euxanthone is unacted on when heated with potash at 150° in a sealed tube.

J. B. T.

Synthesis of Aromatic Mercaptans. By G. Lustig (*Gazzetta*, **21**, 213—216).—Leuckart (Abstr., 1890, 603) has shown that thiophenols may be prepared by the action of potassium ethyl xanthate on diazo-compounds. The author finds it more convenient to employ the red salt, $OH\cdot CS\cdot SK$, obtained by the action of carbon bisulphide on caustic potash in place of potassium ethyl xanthate.

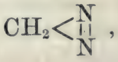
The red salt obtained by digesting 14 grams of solid potassium hydrate with excess of carbon bisulphide, is dissolved in 100 c.c. of water, heated at 70—75°, and a solution of diazobenzene chloride, prepared from 20 grams of aniline, slowly run into it; a yellow substance is thus formed which decomposes into an oil with evolution of nitrogen. The oil is soluble in acetic acid, alcohol, light petroleum, and ether, but insoluble in potash and dilute acids; no analysis could be made, as the oil could not be purified. On steam distillation, it yields thiophenol and diphenyl bisulphide. When boiled with either aqueous or alcoholic potash and treated with acid, the oil yields 65—75 per cent. of thiophenol.

When paramonacetylphenylenediamine is diazotised, and treated with the red salt in the manner just described, a solid product, melting at 115—120°, is formed corresponding with the oil obtained from diazobenzene chloride. This, on hydrolysis with 1 mol. of alcoholic potash, yields paradithioacetylphenylamine, and with 2 mols. paradithiophenylamine, compounds which were recognised by the reactions given by Leuckart.

W. J. P.

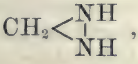
Nomenclature of Compounds containing Two Atoms of Nitrogen Linked together. By T. Curtius (*J. pr. Chem.* [2], **44**, 96—101).—The necessity for a systematic nomenclature for hydrazine derivatives and for fatty diazo-compounds has been evident for some time past, and, with the object of avoiding further confusion, the author proposes to adopt the following means of distinguishing compounds which contain two nitrogen atoms, either singly or doubly linked. The nomenclature is not applicable to the numerous derivatives of hydrazine which contain several carbon atoms united with the two nitrogen atoms in the form of a "ring." (1.) For the radicle $:N\cdot N:$ the term *azi-* is proposed; this being written *-azine* at the end of a word. (2.) For the radicle $\cdot N:N\cdot$ the name *azo-* is retained, but is written *-azone* at the end of a word. (3.) The partial or complete saturation of these radicles by hydrogen is indicated by the prefix *hydr-*, the terms becoming *hydrazi-* or *hydrazo-*, or, at the ends of words, *-hydrazine* or *-hydrazone*, as the case may be. All known azo-, diazo-, and hydrazine-derivatives can readily be distinguished as derivatives either of the as yet unknown hydrazone or diimide, $NH{:}NH$, or of hydrazine, $NH_2{\cdot}NH_2$, and numerous applications of the proposed nomenclature are given in the paper.

The substitution of the azi- and azo-radicles for hydrogen in methane and ammonia would lead to the formation of four 3-membered rings, one of which only has hitherto been isolated, although derivatives of all four have been prepared. These rings are distinguished thus :—



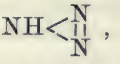
$CH_2<\begin{matrix}N\\ \|\\ N\end{matrix}$,

Azomethylene.



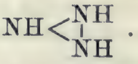
$CH_2<\begin{matrix}NH\\ |\\ NH\end{matrix}$,

Hydrazimethylene.



$NH<\begin{matrix}N\\ \|\\ N\end{matrix}$,

Azoimide.



$NH<\begin{matrix}NH\\ |\\ NH\end{matrix}$.

Hydraziimide.

As an instance of the application of the proposed nomenclature, the change of name from ethyl diazoacetate to ethyl azomethylenecarboxylate may be quoted.

W. P. W.

Action of Benzylamine on Glycol Chlorhydrin. By G. GOLDSCHMIEDT and R. JAHODA (*Monatsh.*, **12**, 81—85).—When molecular proportions of benzylamine and glycol chlorhydrin are heated together at 100° in a reflux apparatus, a vigorous action takes place, and the contents of the flask become dark-red. On cooling, the product solidifies to a yellow, waxy mass, which contains benzylamine hydrochloride and hydroxyethylbenzylamine. On heating the latter with hydrochloric acid at 170° for five hours, it is converted into chlorethylbenzylamine hydrochloride, $CH_2Ph{\cdot}NH{\cdot}CH_2{\cdot}CH_2Cl$, which crystallises in white needles, melts at 192°, and is readily soluble in water, alcohol, and chloroform.

When the yellow, waxy mass is heated in open flasks or closed tubes with sulphuric acid, or with zinc chloride, benzylamine and *benzylmorpholine*, $CH_2Ph{\cdot}N<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}>O$, are produced. The latter crystallises in slender needles, and has an odour resembling that of ammonia; it forms a *hydrochloride*, $C_{11}H_{15}NO,HCl$, which dissolves readily in water and in alcohol, and melts at about 200°; also a *platinochloride*, $(C_{11}H_{15}NO)_2,H_2PtCl_6$, which is only sparingly soluble in water, crystallises in reddish-yellow needles, and decomposes at 192°.

The condensation occurring in the preparation of benzylmorpholine takes place between two hydroxyl groups with elimination of the elements of water, and not between chlorine and hydroxyl, as in the syntheses of morpholine derivatives effected by Knorr (Abstr., 1889, 1218).

G. T. M.

Commercial Pseudocumidine. By H. KRÖMER (*Ber.*, **24**, 2407—2415).—The author's experiments were made with two different specimens of commercial pseudocumidine. The first, melting at 63°, yielded durylonitrile when treated by Sandmeyer's method; whilst the second, melting at a higher temperature, on similar treatment, gave an oil having a strong, phenolic odour, from which durylonitrile and mesitylol, melting at 68—69°, were obtained.

Cumobenzylamine, $C_6H_2Me_3{\cdot}CH_2{\cdot}NH_2$, is formed exclusively on reducing the nitrile from the pseudocumidine melting at 63° by Ladenberg's method with sodium and absolute alcohol. When the reduction is complete, water is added, the solution acidified with hydrochloric acid, the alcohol distilled off, and, after adding an excess of potash, the base is driven over in a current of steam. It crystallises from alcohol in groups of long, friable needles, melts at 64·5°, and is sparingly soluble in hot water, more readily in alcohol and chloroform. The *hydrochloride*, $C_{10}H_{15}N,HCl$, forms short, thick prisms and needles, melts at 240—242° with decomposition, and is fairly soluble in cold water; the *sulphate* forms colourless plates, melts at 238°, and is sparingly soluble in water; the *platinochloride*, $(C_{10}H_{15}N)_2,H_2PtCl_6$, is a reddish-yellow, crystalline powder decomposing at 208—209°; the *mercurochloride*, $C_{10}H_{15}N,HHgCl_3$, crystallises in needles, melts at 141—142°, and is sparingly soluble in cold water, readily in hot; the *picrate*, $C_{10}H_{15}N,C_6H_2(NO_2)_3{\cdot}OH$, separates from hot water in long, yellow needles; the *bismuthoiodide*, $C_{10}H_{15}N,HBiI_4$, is a microcrystalline powder, readily soluble in cold alcohol; whilst the *aurochloride* decomposes on boiling with water.

Cumobenzyl alcohol, $C_6H_2Me_3{\cdot}CH_2{\cdot}OH$, is obtained when a concentrated solution of cumobenzylamine hydrochloride is treated with a slight excess of the theoretical quantity of sodium nitrite in the cold, the solution being finally heated for a short time on the water-bath. The aqueous liquid, on the surface of which a dark-coloured oil floats, is extracted with ether when cold, and the oily residue obtained on distilling the ethereal solution is dissolved in hot alcohol, and repeatedly recrystallised, when the compound is obtained in pale-yellow needles. It melts at 168°, and is almost insoluble in water, more easily in alcohol and ether.

Hemimellibenzylamine, $C_6H_2Me_3{\cdot}CH_2{\cdot}NH_2$, was obtained as chief product from the pseudocumidine of higher melting point, and is isolated in the same manner as cumobenzylamine (see above), but, as it is more soluble in water, the distillate obtained on driving the base over with steam must be extracted with ether. The ethereal solution is distilled, and the crude base converted into the hydrochloride, from which the pure base is obtained on decomposition with potash and crystallisation from hot water. It forms small plates having a silvery lustre, but these change to an amorphous powder when kept in the desiccator, and it then melts at 123°. The *hydrochloride* forms delicate needles, melts at 270°, and is sparingly soluble in cold water and in alcohol; the *platinochloride* separates from hot dilute hydrochloric acid in rhombic dodecahedra and melts at 219—220°; the *aurochloride*, $C_{10}H_{15}N,HAuCl_4$, crystallises from boiling water containing hydrochloric acid in garnet-red prisms, and melts at 162—165° with decomposition; the *mercurochloride* forms a felt-like mass of needles, and melts at 240—241°; whilst the *picrate* separates from alcohol in long, yellow needles, and melts at 239·5° with partial decomposition. Potassium bismuth iodide, potassium cadmium iodide, and iodine dissolved in potassium iodide solution yield sparingly soluble derivatives.

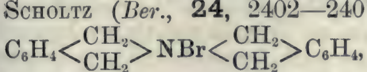
Hemimellibenzyl alcohol, $C_6H_2Me_3{\cdot}CH_2{\cdot}OH$, is prepared from the last-described amido-compound by a process similar to that used for cumobenzyl alcohol (see above); it crystallises from dilute alcohol in long needles, melts at 78°, and is sparingly soluble in water, readily in alcohol and ether.

Hemimellibenzaldehyde, $C_6H_2Me_3\cdot COH$, is obtained when the alcohol is suspended in dilute sulphuric acid, and a dilute solution of the calculated quantity of potassium dichromate dropped in. After remaining at the ordinary temperature for several hours, it is steam distilled, and the solid distillate crystallised from dilute alcohol; it forms needles, melts at 52°, and exhibits all the reactions of an aldehyde.

The nitrile obtained from the pseudocumidine of higher melting point, on hydrolysis with alcoholic potash, gave durylic acid melting at 149—150° and α-isodurylic acid melting at 203°; these were separated by fractional crystallisation of their potassium salts.

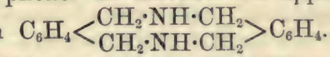
The author has prepared pseudocumidine melting at 63° by treating the commercial substance with nitric acid, as directed by Hofmann, but this yielded (by Sandmeyer's method) mesitylol and a cyanide, from which the two last-mentioned acids were obtained. This can only be explained, if Hofmann's method is trustworthy, by assuming a migration of the methyl groups, but, if otherwise, the commercial base would appear to be a mixture of pseudocumidine and mesidine; hemimellidine must also be considered as a constituent, and, indeed, the latter must have been present in considerable quantity in the above-mentioned commercial base melting at the higher temperature.

A. R. L.

Action of Ammonia on Ortho-xylylene Bromide. By M. SCHOLTZ (*Ber.*, **24**, 2402—2407).—*Di-xylyleneammonium bromide*,  $C_6H_4{<}{}^{CH_2}_{CH_2}{>}NBr{<}{}^{CH_2}_{CH_2}{>}C_6H_4$, is obtained when ortho-xylylene bromide (3 grams) is heated at 120° with 10 times its weight of concentrated ammonia; it forms large, prismatic crystals, is not decomposed when boiled with potassium hydroxide solution, but when shaken with an excess of silver oxide and the filtrate evaporated, deliquescent crystals of the *hydroxide*, $N(C_8H_8)_2\cdot OH$, remain. This has all the properties of an ammonium hydroxide, its solutions having a strongly alkaline reaction, absorbing carbonic anhydride, and liberating ammonia from ammonium chloride on boiling; it furnishes the first example of an ammonium base with two bivalent alcohol radicles. The *aurochloride*, $C_{16}H_{16}N,AuCl_4$, forms delicate needles, melts at 197°, and is very sparingly soluble; the *platinochloride*, $(C_{16}H_{16}N)_2,PtCl_6$, melts at 249°, and is almost insoluble in boiling water; whilst the *mercurochloride* has the composition

$$C_{16}H_{16}NCl,2HgCl_2.$$

The *iodide*, $N(C_8H_8)_2I$, separates when the hydroxide is neutralised with hydriodic acid; it crystallises in long needles, and is much less soluble than the bromide. The *periodide*, $N(C_8H_8)_2I_3$, separates as a brown precipitate when solution of iodine in hydriodic acid is added to an aqueous solution of the iodide; this crystallises from alcohol in violet needles having a metallic lustre; whilst the *perbromide* forms small, golden-yellow plates, and is very unstable.

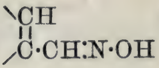
Ortho-xylylene bromide reacts with ammonia, even at 100°; when, however, the temperature is raised above 120°, an oily product yielding a crystalline base on purification is obtained. The latter is advantageously prepared by heating di-xylylene ammonium bromide for eight hours in a sealed tube at 170°. It is a secondary base of the composition C_8H_9N, crystallises from alcohol in long needles, melts at 79—80°, and distils without decomposition between 130° and 135° under a pressure of 12 mm. It forms two *hydrochlorides*, $(C_8H_9N)_2,HCl$ and C_8H_9N,HCl, which are obtained when the base is suspended in water and hydrogen chloride passed through the mixture until the base just dissolves; the *picrate*, $C_8H_9N,C_6H_3N_3O_7$, crystallises in yellow needles; a *hydrobromide*, $(C_8H_9N)_2,HBr$, was also obtained. An *ammonium iodide*, $C_6H_8NMe_2I$, is formed when the base is treated with methyl iodide. The fact that the base forms two series of salts indicates that its molecular formula is twice that above given, and this was confirmed by a determination of the molecular weight by Raoult's method, employing phenol as solvent. It appears, therefore, to have the constitution  $C_6H_4<\begin{matrix}CH_2\cdot NH\cdot CH_2\\CH_2\cdot NH\cdot CH_2\end{matrix}>C_6H_4$.

When either meta- or para-xylylene bromide are heated with ammonia at 100°, a yellow, amorphous, non-nitrogenous substance, containing bromine, is formed; this is insoluble in every solvent which was tried; even when it is purified by washing with acids and alcohol, it did not yield concordant results on analysis. A. R. L.

Ladenburg's Method for Distinguishing Orthodiamines. By G. MAZZARA and A. LEONARDI (*Gazzetta*, **21**, 256).—In the communication an abstract of which appears on p. 1364, it was shown that on heating diamidothymol hydrochloride with benzaldehyde, hydrogen chloride is evolved below 100°, the ortho-position of its hydroxyl relatively to an amido-group allowing it to behave like an orthodiamido-compound, giving rise to a benzenyl derivative. Diamidocarvacrol hydrochloride [Me : OH : NH_2,HCl : Pr : NH_2,HCl = 1 : 2 : 3 : 4 : 5] and orthamidophenol hydrochloride also evolve hydrogen chloride on heating at 100° with benzaldehyde, probably owing to the formation of the corresponding benzenyl derivatives. Ladenburg's criterion for orthodiamines (Abstr., 1878, 571), which depends on the evolution of hydrogen chloride on heating with benzaldehyde at 100°, is, therefore, not characteristic of those compounds, and is satisfied by orthamidophenols, and by those diamidophenols which have the hydroxyl groups in the ortho-position with respect to an amido-group.

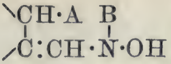
S. B. A. A.

Constitution of Isomeric Oximes. By G. MINUNNI (*Gazzetta*, **21**, 113—136).—The author criticises adversely the current theories of the isomerism of oximes, and considers that the isomerism may be satisfactorily explained without the assumption of space formulæ; he regards the conversion of one oxime into its isomeride as due to the formation and subsequent decomposition of an intermediate additive product with the agent producing intramolecular change. Thus the conversion of α- into β-benzaldoxime may be represented as follows:—



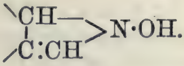
$$\begin{array}{l}\diagdown CH \\ \;\| \\ \diagup C{\cdot}CH{:}N{\cdot}OH\end{array}$$

α-group.



$$\begin{array}{l}\diagdown CH{\cdot}A\;\;B \\ \;\;| \qquad\; | \\ \diagup C{:}CH{\cdot}N{\cdot}OH\end{array}$$

Intermediate product.



$$\begin{array}{l}\diagdown CH\text{—} \\ \;\;| \qquad\quad >N{\cdot}OH. \\ \diagup C{:}CH\end{array}$$

β-group.

The existence of α-, β-, and γ-benzildioximes is explained in a similar manner.

The absence of isomerides among the fatty oximes is attributed to the unfavourable distribution of the atomic bonds among the carbon atoms contiguous to the oximido-group. W. J. P.

Note.—A reply to this paper has been published by Hantzsch (this vol., p. 823), and Cramer has obtained isomeric oximidosuccinic acids (this vol., p. 824). W. J. P.

Action of Hydrazine Hydrate on Ketones and Orthodiketones. By T. Curtius and K. Thun (*J. pr. Chem.* [2], **44**, 161—186).—When hydrazine hydrate (1 mol.) is added to a ketone (2 mols.), derivatives of azimethylene, $CH_2{\cdot}N{:}N{\cdot}CH_2$, ketazines, are obtained; these compounds are more stable on heating, or when heated with reducing agents, than the aldazines (Abstr., 1889, 393), but less so with dilute acids; they are not decomposed by hot alkalis, do not reduce Fehling's solution, and only act on ammoniacal silver solution on protracted boiling (see below).

Bidimethylazimethylene, $CMe_2{:}N{\cdot}N{:}CMe_2$, is obtained by gradually adding hydrazine hydrate (10 grams) to cooled acetone (22 grams). The product is dried over potash and fractionated, when nearly the whole passes over at 131°, the yield being 16·5 grams. It is a transparent, highly refractive liquid of a penetrating odour, and has a sp. gr. of 0·8365 at 21·5°; it is miscible in all proportions with water, alcohol, and ether; mineral acids and also picric acid decompose it in the cold into hydrazine and acetone.

Bimethylethylazimethylene, $CMeEt{:}N{\cdot}N{:}CMeEt$, is formed on adding hydrazine hydrate (10 grams) to methyl ethyl ketone (27 grams); heat is developed, causing the mixture to boil; it is purified as in the case of the dimethyl derivative. It boils at 167—172° (at 75° under a pressure of 12 mm.), and closely resembles the dimethyl derivative, but has a less intense odour, and is more sparingly soluble in water; its sp. gr. is 0·8335 at 24°.

Bimethylpropylazimethylene, $CMePr{:}N{\cdot}N{:}CMePr$, is prepared from methyl propyl ketone. It boils at 195—200° (at 95° under a pressure of 12 mm.), is sparingly soluble in water, and has an odour recalling that of peppermint; its sp. gr. is 0·8335 at 24°.

Bimethylhexylazimethylene, $C_6H_{13}{\cdot}CMe{:}N{\cdot}N{:}CMe{\cdot}C_6H_{13}$, prepared from methyl hexyl ketone, is a pale-yellow oil of a basic odour; its sp. gr. is 0·8300 at 24°, and it boils at 286—290° (at 150° under a pressure of 12 mm.).

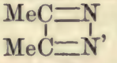
Bidiethylazimethylene, $CEt_2{:}N{\cdot}N{:}CEt_2$, from diethyl ketone, boils at 190—195° (at 92° under a pressure of 12 mm.). Its odour resembles that of the dimethyl derivative, and its sp. gr. is 0·836 at 24°.

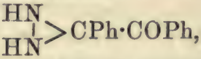
Bimethylphenylazimethylene, $CMePh{:}N{\cdot}N{\cdot}CMePh$, formed when hydrazine hydrate is heated with acetophenone in a sealed tube at

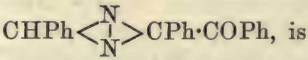
100° for 12 hours. The solid product when crystallised from alcohol yields anisotropic prisms. It melts at 121°, boils above 360° without decomposition, and is easily soluble in hot alcohol, sparingly in cold, and insoluble in water.

Curtius has already suggested (Abstr., 1889, 1157) that the compounds obtained from benzile and hydrazine hydrate probably contain the group NH·NH, and the present experiments support this. The authors have now submitted these compounds to a closer examination, and regard them as derivatives of hydrazimethylene; they have also studied similar derivatives of other orthodiketones (compare also this vol., p. 1350).

Dimethylbihydrazimethylene, $N_2H_2{:}CMe{\cdot}CMe{:}N_2H_2$, is produced by gradually adding hydrazine hydrate (2·5 grams) to diacetyl (2 grams) with cooling. When half the hydrate has been added, the melt solidifies, probably owing to the formation of the monhydrazi-derivative, so that it is necessary to heat the mixture whilst the rest of the hydrazine is being added. The solid product crystallises from alcohol in colourless, lustrous prisms, melts at 158°, and is very easily soluble in hot alcohol, sparingly in cold water and in benzene. Its aqueous solution has a neutral reaction, and, on addition of silver nitrate, yields a silver salt which quickly reduces; the compound is decomposed by acids in the cold, but is very stable towards alkalis; it reduces Fehling's solution in the cold.

Dimethylaziethane,  $\begin{array}{l}MeC{=}N\\ \;\,|\quad\;|\\ MeC{=}N\end{array}$, is obtained when hydrazine hydrate acts on diacetyl in molecular proportion, and is of interest as the first example of a compound formed by the condensation of 1 mol. of hydrazine with two ketonic groups. It separates from boiling benzene as a dull-yellow, microscopic powder, melts at 270°, and is sparingly soluble in boiling alcohol and benzene, and almost insoluble in water; it becomes electrical when rubbed.

Benzoylphenylhydrazimethylene,  $\begin{array}{l}HN\\ \;|\\ HN\end{array}{>}CPh{\cdot}COPh$, is formed from hydrazine hydrate and benzile in molecular proportion; hydrazine hydrate (6 grams) is added to a hot alcoholic solution of benzile (20 grams), and the mixture boiled for some minutes. The product (20 grams) is collected and washed with alcohol; it forms white, crystalline scales, melts at 151° with decomposition, and is sparingly soluble in cold water, easily in hot alcohol. When distilled under a pressure of 30 mm., it boils at 220°, and yields a distillate solidifying to a crystalline mass, which was identified as phenyl benzyl ketone (deoxybenzoïn).

Benzoylisobenzaldazine,  $CHPh{<}\begin{array}{c}N\\ |\\ N\end{array}{>}CPh{\cdot}COPh$, is produced when benzaldehyde is heated with twice its weight of benzoylphenylhydrazimethylene on the water-bath for a short time; the viscid product soon becomes crystalline, and is spread on a tile, and crystallised from benzene, when it is obtained in large, nodular aggregates; it is deposited from boiling alcohol in small, yellow, lustrous prisms, melts at 150°, and boils with decomposition at 300° under a pressure of 80 mm. It is insoluble in water, sparingly soluble in boiling alcohol, and easily in boiling benzene.

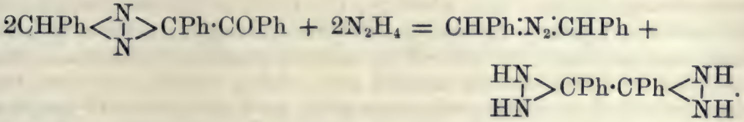
When a mixture of benzoylisobenzaldazine (10 grams) and hydrazine hydrate (2 grams; 1 mol.), moistened with alcohol, is heated in a sealed tube for 4—5 hours, white needles melting at 131—139°, and a clear oil having an odour recalling that of soap-lye, are obtained; the former, on repeated crystallisation from boiling benzene, yields benzoylphenylhydrazimethylene, and a compound melting at 147° which is perhaps diphenylbihydrazimethylene; the formation of tolane on oxidation was not, however, observed with this (see below); whilst the oil, which contains the benzalhydrazine

$$\mathrm{CHPh{:}N{\cdot}NH_2},$$

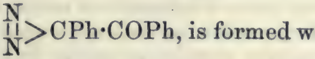
on boiling for a short time with cinnamaldehyde, is converted into *cinnamalbenzaldazine*, $\mathrm{CHPh{:}N_2{:}CH{\cdot}CH{\cdot}CHPh}$; this crystallises from alcohol in yellow needles and melts at 114°. The benzalhydrazine is a very unstable compound, and decomposes in the presence of water even in the cold into benzaldazine and hydrazine, thus:—

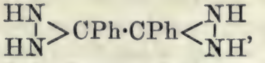
$$2\mathrm{CHPh{:}N{\cdot}NH_2} = \mathrm{CHPh{:}N_2{:}CHPh} + \mathrm{N_2H_4}.$$

The action of hydrazine hydrate on benzoylisobenzaldazine is therefore probably represented thus:—

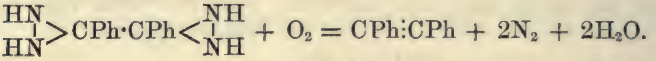


$$2\mathrm{CHPh}<\begin{matrix}\mathrm{N}\\|\\\mathrm{N}\end{matrix}>\mathrm{CPh{\cdot}COPh} + 2\mathrm{N_2H_4} = \mathrm{CHPh{:}N_2{:}CHPh} + \begin{matrix}\mathrm{HN}\\|\\\mathrm{HN}\end{matrix}>\mathrm{CPh{\cdot}CPh}<\begin{matrix}\mathrm{NH}\\|\\\mathrm{NH}\end{matrix}.$$

Benzoylphenylazomethylene,  $\begin{matrix}\mathrm{N}\\\|\\\mathrm{N}\end{matrix}>\mathrm{CPh{\cdot}COPh}$, is formed when benzoylphenylhydrazimethylene is suspended in benzene and shaken for half an hour with the calculated quantity of mercuric oxide; the orange solution is decanted from the mercury, evaporated, and the compound crystallised from ether, when it is obtained in orange-red, transparent tablets; the yield is quantitative; it melts at 63° with decomposition, and also decomposes when boiled with water or when treated in the cold with mineral acids or an alcoholic solution of iodine.

Diphenylbihydrazimethylene,  $\begin{matrix}\mathrm{HN}\\|\\\mathrm{HN}\end{matrix}>\mathrm{CPh{\cdot}CPh}<\begin{matrix}\mathrm{NH}\\|\\\mathrm{NH}\end{matrix}$, is prepared by heating benzile (5 grams) with hydrazine hydrate (3 grams) in a sealed tube at 100° for 10 hours. The product crystallises from alcohol in long, colourless needles, melts at 147°, and decomposes at 190°; it remains unaltered on exposure to the air or light, but is decomposed by acids in the cold. When boiled with acetic anhydride, it yields a colourless powder which melts at 238°.

Asymmetrical dibenzylazine, $\mathrm{CH_2Ph{\cdot}CPh{:}N{\cdot}N{:}CPh{\cdot}CH_2Ph}$, is obtained when diphenylbihydrazimethylene is heated for 12 hours at 200° under reduced pressure; on adding alcohol to the greenish, oily product, a yellow powder separates; this is collected, washed with alcohol, and crystallised from boiling alcohol, when it forms lustrous, yellow needles which melt at 161—162°. It is sparingly soluble in boiling alcohol, readily in benzene, and insoluble in boiling water. The compound gives a white precipitate with silver nitrate, and it is not attacked when its solution in benzene is boiled with mercuric oxide. When dibenzylazine is boiled with sulphuric acid, it is hydrolysed, phenyl benzyl ketone passing over with the steam, whilst hydrazine sulphate remains behind. When diphenylbihydrazimethylene is suspended in benzene and treated with mercuric oxide, it yields tolane, thus:—



$$\left.\begin{matrix}HN\\|\\HN\end{matrix}\right>CPh\cdot CPh\left<\begin{matrix}NH\\|\\NH\end{matrix}\right. + O_2 = CPh\vdots CPh + 2N_2 + 2H_2O.$$

A. R. L.

Action of Hydrazine Hydrate on Benzophenone. By T. Curtius and F. Rauterberg (*J. pr. Chem.* [2], **44**, 192—207).—The compound obtained from hydrazine hydrate and benzophenone exhibits no analogy to the derivatives prepared by Curtius and Thun from other ketones (preceding abstract); the authors conclude from its general reactions that it contains the group N·NH (see below).

Diphenylmethylenehydrazine, $CPh_2{:}N\cdot NH_2$, is obtained by heating hydrazine hydrate (1·8 grams) with benzophenone (5 grams) and absolute alcohol (1 gram) in a sealed tube at 150° for six hours, and crystallising from a little alcohol; the yield is almost quantitative. It forms stout prisms several centimetres in length, melts at 98°, and boils undecomposed at 225—230° under a pressure of 55 mm. It is insoluble in water and in alkalis, but readily soluble in ether, benzene, hot alcohol, dilute sulphuric acid, and glacial acetic acid; on adding an alkali to its solution in acids, it is reprecipitated. It yields a metallic mirror when heated with alcoholic silver solution, but only produces a slight reduction with Fehling's solution; after being heated with dilute sulphuric acid, however, the latter is immediately reduced. The molecular weight determinations by Raoult's method, employing benzene as solvent, gave a mean value of 181·8. When the base is mixed with an excess of dilute sulphuric acid and steam distilled, ether extracts benzophenone from the distillate, whilst hydrazine sulphate can be obtained from the residue. The *hydrochloride*, $CPh_2N_2H_2,HCl$, may be prepared by passing dry hydrogen chloride into an ethereal solution of the base; it forms white needles, melts at 183°, and is very readily soluble in water; it decomposes in aqueous solution, or in the dry state when exposed to the air, yielding bidiphenylazimethylene (see below); the *nitrite*, obtained by passing nitrous acid into an ethereal solution of the base, decomposes in a manner similar to the hydrochloride. The *acetyl derivative*, $CPh_2{:}N\cdot NHAc$, prepared by treating the base (2 grams) with acetic anhydride (0·8 gram), separates from ether in white prisms, melts at 107°, and is easily soluble in alcohol, ether, and benzene; it is not attacked when its benzene solution is boiled with mercuric oxide, and the compound remains unaltered when heated with acetic anhydride at 150°. The *benzoyl derivative*, $CPh_2{:}N\cdot NHBz$, obtained by gently heating the base with benzoic chloride, crystallises in colourless prisms, melts at 116·5°, and is readily soluble in alcohol and ether.

Bidiphenylazimethylene or *diphenylketazine*, $CPh_2:N\cdot N:CPh_2$, is best prepared by treating diphenylmethylenehydrazine (3 grams) with a solution of iodine (2 grams) in alcohol (10 grams), washing the product with alcohol, and crystallising two or three times from absolute alcohol. It forms small, bright yellow, transparent prisms, melts at 162°, distils undecomposed, and is somewhat sparingly soluble in boiling alcohol, more readily in ether and benzene, but insoluble in alkalis and ammonia. Molecular weight determinations by Raoult's method, employing benzene as solvent, gave a mean value of 317·9. When boiled with dilute sulphuric acid for three hours, the compound dissolves, and on steam distilling the solution, benzophenone passes over, whilst hydrazine sulphate remains in the residue. Bidiphenylazimethylene is also formed when diphenylmethylenehydrazine is distilled under diminished pressure. $2CPh_2:N\cdot NH_2 = CPh_2:N\cdot N:CPh_2 + N_2H_4$ (see also below).

Diphenylmethylenetetrazone, $CPh_2:N\cdot N:N\cdot N\cdot CPh_2$, is obtained by allowing a cooled solution of diphenylmethylenehydrazine to remain in contact with somewhat more than the calculated quantity of mercuric oxide for 24 hours, shaking at intervals. The solution, which first acquires a yellow colour and then becomes red, is quickly evaporated to dryness by a current of air; the residual deep-red oil solidifies to a mass of needles when cooled. The compound, which melts at the temperature of the room, is readily soluble in alcohol, ether, and benzene. On exposure to the air for several days, either by itself or in benzene solution, it decomposes into diphenylketazine and nitrogen; this decomposition is effected in a few hours when the benzene solution is boiled. Diphenylketazine is likewise produced when the tetrazone is treated with iodine, bromine, or hydrogen chloride in an indifferent solvent. If, however, a benzene solution of the tetrazone is treated with hydrogen bromide, diphenylketazine separates and is removed, whilst the filtrate on evaporation in a vacuum yields an oil which soon solidifies; this, after crystallisation from ether, forms colourless prisms, melts at 38°, and is readily soluble in benzene, ether, and alcohol; it was proved to be diphenylbromomethane, which, according to Friedel and Balsohn (Abstr., 1880, 558), melts at 45°.

Diphenylmethylenebenzaldazine, $CPh_2:N\cdot N:CHPh$, is formed with development of heat when diphenylmethylenehydrazine (2 grams) and benzaldehyde (1·1 grams) are mixed, or better when the two are shaken together in molecular proportion in the presence of a few drops of alkali; it crystallises from alcohol in tufts of sulphur-yellow needles, melts at 75° with partial decomposition, and is readily soluble in ether and alcohol, but insoluble in water. *Diphenylmethylenecinnamaldazine*, $CPh_2:N\cdot N:CH\cdot CH:CHPh$, is prepared in the same manner from diphenylmethylenehydrazine and cinnamaldehyde; it forms lemon-yellow needles, melts at 98°, and is readily soluble in alcohol, ether, and benzene. Diphenylmethylenehydrazine and chloral react with formation of diphenylketazine.

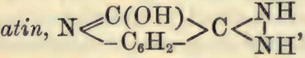
Diphenyldimethylazimethylene, $CPh_2:N\cdot N:CMe_2$, is obtained on heating diphenylmethylenehydrazine (3 grams) with acetone (1 gram) for an hour on the water-bath in a reflux apparatus; the oily product solidifies, and on being crystallised from ether forms yellowish-green crystals, melts at 60·5°, is readily soluble in alcohol, ether, and benzene, and remains unaltered when its solution in benzene is boiled with mercuric oxide.

Diphenylmethylcinnamaldazimethylene, $CPh_2{:}N{\cdot}N{:}CMe{\cdot}CH{:}CHPh$, is formed from diphenylmethylenehydrazine and benzylidineacetone; it separates from ether in yellow prisms, melts at 126°, and is readily soluble in alcohol, but insoluble in water.

Diphenylmethylphenylazimethylene, $CPh_2{:}N{\cdot}N{:}CMePh$, is prepared by heating diphenylmethylenehydrazine with acetophenone in a sealed tube at 160° for six hours; it crystallises from alcohol in lustrous, golden-yellow prisms, melts at 105°, distils without decomposition, and is readily soluble in ether, alcohol, and benzene. Bidiphenylazimethylene (diphenylketazine), $CPh_2{:}N{\cdot}N{:}CPh_2$ (see above), is formed when diphenylmethylenehydrazine and benzophenone are heated together in molecular proportion in a sealed tube at 150°.

A. R. L.

Action of Hydrazine Hydrate on Isatin and Phenols. By T. CURTIUS and K. THUN (*J. pr. Chem.* [2], **44**, 187—191).—*Hydrazisatin*,



$N{\lessgtr}\begin{array}{c}C(OH)\\ -C_6H_2-\end{array}{>}C{<}\begin{array}{c}NH\\ |\\ NH\end{array}$,

is obtained when isatin (20 grams) is dissolved in hot absolute alcohol (200° c.c.), hydrazine hydrate (7 grams) added, and the mixture boiled for an hour. When cold, the product is collected, washed with alcohol, and recrystallised from the same solvent. It separates from boiling water in pale-yellow needles, or from boiling alcohol in dull, straw-yellow plates, melts at 219°, and is very sparingly soluble in boiling water, alcohol, ether, and benzene. It behaves both as an acid and a base. On adding silver nitrate to its ammoniacal solution, a red salt separates which darkens quickly, but on boiling its aqueous solution with silver nitrate, a metallic mirror is produced. It is decomposed by boiling with mineral acids, and its solution in sodium hydroxide gives a yellow precipitate with Fehling's solution. When hydrazisatin is distilled under a pressure of 90 mm., it boils at 255°, and oxindole passes over; the yield after redistilling under a pressure of 73 mm. (b. p. 227°) is 60 per cent. When a solution of hydrazisatin in benzene is boiled with mercuric oxide, an *azo-derivative* is obtained as a brownish-red powder which deflagrates on heating.

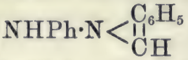
Phenoldiammonium, $N_2H_4Ph{\cdot}OH$ (?), is formed when hydrazine hydrate is poured over dry phenol; it melts at 55—57°, but decomposes even when dried in the desiccator, and could not therefore be analysed.

Hydrazine hydrate acts with explosive violence on quinone with the formation of quinol, which then becomes converted into quinoldiammonium.

Quinoldiammonium, $N_2H_4C_6H_4(OH)_2$, is precipitated in white plates when hydrazine hydrate (3 grams) is slowly added to quinol (3·5 grams) dissolved in ether. It is collected, washed with ether, and crystallised from boiling alcohol; it separates in thick, white crystals, melts at 154° with decomposition, and is readily soluble in water (the yield is 6 grams). It is very unstable, and decomposes after keeping for some months; it reduces Fehling's solution in the cold,

and when its aqueous solution is shaken with benzaldehyde, benzaldazine is produced.
A. R. L.

Action of Phenylhydrazine on the Benzaldoximes. By G. MINUNNI and L. CABERTI (*Gazzetta*, **21**, 136—142).—When either α- or β-benzaldoxime is heated at a little above 100° for some hours with an equal weight of phenylhydrazine, the hydrazone obtained is identical with that prepared by E. Fischer by the direct action of phenylhydrazine on benzaldehyde, and melts at 156—157°, and not at 152·5° as stated by Fischer. The lower melting point is caused by the presence of impurity.

In view of Minunni's explanation of the isomerism of the benzaldoximes (this vol., p. 1354), it is supposed that two isomeric hydrazones are initially formed from the isomeric oximes, but that the β-hydrazone, to which the constitution  $\mathrm{NHPh{\cdot}N}{<}\begin{matrix}\mathrm{C_6H_5}\\ \Vert \\ \mathrm{CH}\end{matrix}$ is assigned, undergoes intramolecular change at the moment of formation, and is converted into the stable α-hydrazone, $NHPh{\cdot}N{:}CHPh$.

A further investigation of this reaction is being carried on.
W. J. P.

Nitrohalogenhydrazo- and Nitrosohalogenazo-compounds. By C. WILLGERODT and L. ELLON (*J. pr. Chem.* [2], **44**, 67—77).—Orthonitroallometachlorophenyl-phenylhydrazine,

$$NHPh{\cdot}NH{\cdot}C_6H_3Cl{\cdot}NO_2,$$

is best prepared by boiling an alcoholic solution of Laubenheimer's dinitrochlorobenzene (9 grams) and phenylhydrazine (9·6 grams), and afterwards allowing it to remain in the cold for 24 hours (Willgerodt and Ferko, Abstr., 1888, 830). When reduced by boiling with alcoholic ammonium sulphide for two days, or by boiling with acetic acid, it is converted into orthonitrosoallometachlorophenylazobenzene, melting at 142·5°, not at 136—137° as previously stated (*loc. cit.*). On treatment with the calculated quantity of bromine in chloroform solution (10 grams of bromine in 100 c.c. of the solution) at the boiling point for three hours, it yields *orthonitrosoallometachlorodibromophenylazobenzene*, $C_{12}H_6ClBr_2N_2{\cdot}NO$, which crystallises in lustrous, red needles melting at 143—144°. When oxidised with chromic acid in acetic acid solution, the hydrazine is readily converted into *orthonitroallometachlorazobenzene*, which, on boiling with twice its weight of nitric acid (sp. gr. = 1·48) for 10—12 hours in a reflux apparatus, yields *dinitrochlorazobenzene*, $C_{12}H_7ClN_2(NO_2)_2$, crystallising in red needles melting at 75°, and on boiling with six times its weight of a mixture of fuming nitric acid and concentrated sulphuric acid in equal proportions, yields *trinitrochlorazobenzene*, $C_{12}H_6ClN_2(NO_2)_3$, melting at 121°.

Picrylparabromophenylhydrazine, $C_6H_4Br{\cdot}NH{\cdot}NH{\cdot}C_6H_2(NO_2)_3$, is formed when an alcoholic solution of parabromophenylhydrazine (2 mols.) and picryl chloride (1 mol.) is heated to the boiling point. It crystallises in beautiful, yellowish-red, hexagonal forms, melts at 185—186°, and is soluble in almost all organic solvents. When boiled with acetic acid for many hours in a reflux apparatus, it is reduced to dinitronitrosophenylparabromazobenzene (Willgerodt, this vol., p. 689), and when heated with alcohol at 130—140° for three hours, it is further reduced to *dinitrosonitrophenylparabromazobenzene*, $C_6H_4Br\cdot N_2\cdot C_6H_2(NO)_2\cdot NO_2$, which crystallises in yellow needles melting at 241°. On oxidation with chromic acid, the hydrazine is converted into trinitrophenylparabromazobenzene, a compound already prepared by the bromination of picrylphenylhydrazine.

Orthoparadinitrophenylparabromophenylhydrazine,

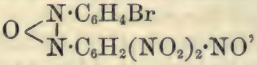
$$C_6H_4Br\cdot NH\cdot NH\cdot C_6H_3(NO_2)_2,$$

is obtained by boiling an alcoholic solution of α-dinitrochlorobenzene (5 grams) with parabromophenylhydrazine (10 grams) in a reflux apparatus for some hours. It crystallises in small, dark-brown needles, melts at 147—148°, and dissolves in hot benzene, but only sparingly in other organic solvents. When boiled with acetic acid for about five hours, it is reduced to *nitronitrosophenylparabromazobenzene*, $C_6H_4Br\cdot N_2\cdot C_6H_3(NO)\cdot NO_2$, crystallising in yellow needles, which melt at 242°. When heated with alcohol at 150° for three hours, it is further reduced to *dinitrosophenylparabromazobenzene*,

$$C_6H_4Br\cdot N_2\cdot C_6H_3(NO)_2\,;$$

this crystallises in yellowish-brown needles, melts at 222°, and is easily soluble in the ordinary organic solvents. On oxidation with chromic acid in acetic acid solution, the hydrazine is converted into *orthoparadinitrophenylparabromazobenzene*, $C_6H_4Br\cdot N_2\cdot C_6H_3(NO_2)_2$, which crystallises in slender red needles, melts at 175°, and dissolves readily in the ordinary organic solvents.

Orthonitrosoallometachlorophenylazobenzene is not affected by boiling either with alkaline potassium ferricyanide for 8 hours, or with a solution of chromic acid in acetic acid. A compound of the same composition, $C_{12}H_8ClN_3O$, but melting at 121°, is obtained when it is boiled for 8 hours with dilute nitric acid (sp. gr. = 1·12).

Dinitronitrosophenylparabromazobenzene, when boiled with chromic acid in acetic acid solution for about an hour, is oxidised to *dinitronitrosophenylparabromazoxybenzene*,  $O<\begin{matrix}N\cdot C_6H_4Br\\ |\\ N\cdot C_6H_2(NO_2)_2\cdot NO\end{matrix}$, melting at 170·5°.

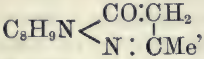
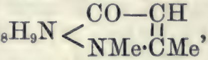
Dinitrosonitrophenylparabromazobenzene under like conditions is oxidised to *dinitrosonitrophenylparabromazoxybenzene*, $C_{12}H_6BrN_5O_6$, melting at 219°.

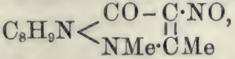
When dinitrosophenylparabromazobenzene is boiled with a solution of chromic acid in acetic acid solution for two hours, it yields *dinitrosophenylparabromazoxybenzene*, $C_{12}H_7BrN_4O_3$, melting at 202°.

W. P. W.

α-Metaxylylhydrazine. By A. Klauber (*Monatsh.*, **12**, 211—220; compare Abstr., 1890, 1410).—α-Metaxylylhydrazine is deposited from its aqueous solution on the addition of supersaturated brine; it does not yield a crystalline compound with carbon bisulphide, and explodes when heated in a vacuum; on exposing a benzene solution of the hydrazine to the atmosphere, a characteristic deep-green coloration is produced, which may serve as a qualitative test. The *hydrochloride* crystallises with 2 mols. H_2O in small, colourless needles, which rapidly become brown on exposure to air.

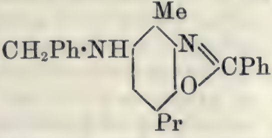
The hydrazine combines with 2 mols. of ethyl acetoacetate when the two are heated together for an hour at 110—120°, and then for two hours at 140—150°. The product, which has the formula $C_{32}H_{34}N_4O_4$, is deposited from alcohol in small crystals, and melts at 203°. It dissolves sparingly in xylene or alcohol, is insoluble in water, ether, and benzene, and does not react with phosphorus pentachloride when heated with it at 180°. With acids, it forms salts which are dissociated on the addition of water.

α-Metaxylylmethylpyrazolone,  $C_8H_9N<\begin{matrix}CO\cdot CH_2\\ N : CMe\end{matrix}$, is obtained by treating the preceding compound with sodium in alcoholic solution, or by heating it with dilute alkalis or acids at 140—150° for two hours in a sealed tube. It crystallises from water containing sodium chloride in concentric needles which melt at 159°. The pyrazolone resembles the corresponding compound from phenylhydrazine, and forms salts with both acids and bases; with ferric chloride, a violet-red coloration is obtained, whilst alkaline copper solutions are readily reduced. The *hydrochloride* is deposited in nodules consisting of prismatic crystals; it melts at 185°. The *ferrocyanide* is sparingly soluble, and quickly undergoes decomposition when heated. On heating the above described condensation product of metaxylylhydrazine and ethyl acetoacetate for two hours at 130° with hydrogen chloride or methyl iodide in methyl alcoholic solution in a sealed tube, *α-metaxylyl-2-3-dimethylpyrazolone* (*xylylantipyrine*),  $C_8H_9N<\begin{matrix}CO—CH\\ NMe\cdot CMe\end{matrix}$, is produced. After purification, it crystallises from light petroleum in small, colourless needles, and melts at 113°. It is readily soluble in alcohol, ether, and benzene, and also in cold water, but on heating an aqueous solution the compound separates as a viscid liquid. The *hydrochloride* crystallises with 2 mols. H_2O in long prisms, which decompose at 112°; the anhydrous salt melts at 95°.

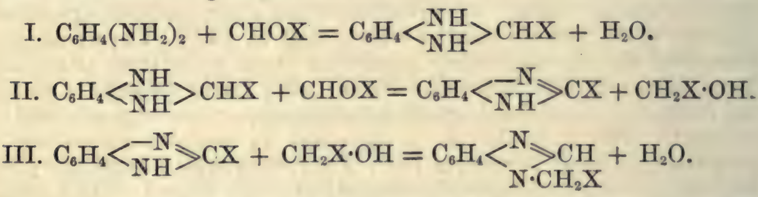
By the action of alkaline nitrites on the hydrochloride, the *nitroso-derivative*,  $C_8H_9N<\begin{matrix}CO - C\cdot NO\\ NMe\cdot CMe\end{matrix}$, is formed; this crystallises from a mixture of alcohol and ether in lustrous, green, metallic needles. The compound has basic properties, and dissolves in acids, but is precipitated from these solutions on the addition of alkalis.

J. B. T.

Behaviour of Aldehydes with Orthamidophenols. By G. Mazzara and A. Leonardi (*Gazzetta*, 21, 251—256.)—*Benzileamidobenzamidothymol*,



is prepared by heating benzaldehyde (8 grams) with diamidothymol hydrochloride in an oil-bath for 10 hours. The reaction commences below 100° with evolution of hydrogen chloride, and is completed on raising the temperature to 120—130°. The product, after purification and repeated recrystallisation from boiling alcohol, separates in long, silky, yellowish-white needles, and melts at 152°. The base also crystallises from light petroleum in small, yellow rhombohedra. It is very soluble in benzene, forming a feebly fluorescent solution. It is insoluble in alkaline hydrates and dilute acids, and is not decomposed by them even on heating. The *hydrochloride* crystallises from hot alcohol in brilliant, white scales, very sparingly soluble in boiling water. The same compound is obtained by heating amidobenzamidothymol with benzoic chloride. The formation of this benzilebenzenyl derivative leads the author to conclude that the reaction between aldehydes and diamido-derivatives of aromatic hydrocarbons takes place in the following stages:—



$$\text{I. } C_6H_4(NH_2)_2 + CHOX = C_6H_4<\substack{NH\\NH}>CHX + H_2O.$$

$$\text{II. } C_6H_4<\substack{NH\\NH}>CHX + CHOX = C_6H_4<\substack{-N\\NH}\gg CX + CH_2X\cdot OH.$$

$$\text{III. } C_6H_4<\substack{-N\\NH}\gg CX + CH_2X\cdot OH = C_6H_4<\overset{N}{\underset{N\cdot CH_2X}{}}\gg CH + H_2O.$$

With the fatty aldehydes, the reaction is limited for the most part to the second stage. S. B. A. A.

Oxidation of Mixed Fatty Aromatic Ketones by Potassium Permanganate. By A. Claus and W. Neukranz (*J. pr. Chem.* [2], **44**, 77—85).—Contrary to the experience of Claus (Abstr., 1890, 769), Glücksmann has shown (Abstr., 1890, 1416) that acetophenone can be oxidised by potassium permanganate with the production of phenylglyoxylic acid if an alkaline solution is employed. The conjecture of Glücksmann that the failure to oxidise the ketone was due to the use of a neutral solution is erroneous, since not only neutral but acid and alkaline solutions were employed, and the oxidation in the presence of alkali was conducted, both in concentrated and dilute aqueous solutions, hot, cold, and at intermediate temperatures. Claus, however, always added the whole quantity of alkali to the ketone prior to the addition of the potassium permanganate, whereas Glücksmann rendered the solution of permanganate alkaline, and treated the ketone with successive quantities of the mixture. The authors find that the difference in the two results is to be referred to this slight difference in procedure, and quote experimental data showing that the quantity of alkali within certain limits, like the concentration and temperature of the solution, is of subsidiary importance compared with the manner in which it is added; they conclude therefore that under Glücksmann's conditions, and no others, is it possible to oxidise acetophenone by potassium permanganate.

Paratolyl methyl ketone, on oxidation at 70° with a solution containing 12 grams of caustic potash and 32 grams of potassium permanganate in 200 c.c. of water, yields 70 per cent. of the theoretical quantity of paratolylglyoxylic acid. This ketone is more readily oxidised to the ketonecarboxylic acid than acetophenone, and small quantities of paratolylglyoxylic acid are even formed when the old method of oxidation in an ice-bath is employed, and the whole quantity of alkali added prior to the addition of the permanganate solution. Orthoxylyl methyl ketone and orthocymyl methyl ketone also yield α-ketonecarboxylic acids on oxidation with potassium permanganate by Glücksmann's method, but details are reserved for a later communication.

Glücksmann's method of oxidation has been applied in the case of ketones which yield α-ketonecarboxylic acids under the old conditions, but experiments with naphthyl methyl ketone, and with mixed aromatic ethyl, propyl, and isopropyl ketones show that neither the nature nor yield of the respective products is altered thereby.

W. P. W.

Paratolylacetic Acid. By A. Claus and R. Wehr (*J. pr. Chem.* [2], **44**, 85—95).—Paratolylacetic acid is best prepared from paratolyl methyl ketone by Willgerodt's reaction (Abstr., 1888, 476). The ketone is heated with an excess of saturated ammonium sulphide and about 40 per cent. of its weight of powdered sulphur at 250° for 5—6 hours, and the resulting paratolylacetamide boiled with an equal weight of caustic potash and 10—20 times its weight of water for 6—8 hours until ammonia is no longer evolved; the acid is then precipitated in slender, colourless needles on the addition of a mineral acid to the solution. It sublimes in needles without decomposition, melts at 92° (uncorr.), and is easily soluble in alcohol, ether, chloroform, and hot water, but only sparingly in cold water. The lower melting point of 74° previously given (Claus and Kroseberg, Abstr., 1887, 949) was obtained with an impure material, which, on subsequent purification, has been found to melt at 91°. On oxidation with boiling dilute nitric acid (sp. gr. = 1·15), it yields paratoluic acid; with concentrated nitric acid, a mixture of terephthalic acid with nitro-derivatives; and with either chromic acid or potassium permanganate in quantity corresponding with three atomic proportions of oxygen, a mixture of paratoluic acid with a small amount of terephthalic acid.

Metanitroparatolylacetic acid, $NO_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}COOH$, is obtained when a solution of paratolylacetic acid in five times its weight of nitric acid (sp. gr. = 1·52) is allowed to remain in the cold for 14—21 days. It crystallises from water in colourless, transparent, glassy needles, sublimes in small, colourless needles, melts at 102°, and dissolves very sparingly in cold water, but easily in alcohol, ether, carbon bisulphide, &c. On oxidation in alkaline solution with an amount of potassium permanganate corresponding with three atomic proportions of oxygen, it is converted into metanitroparatoluic acid. The *sodium* salt, with $2\frac{1}{2}$ mols. H_2O, crystallises in small, flat needles, and is very soluble in water; the *barium* salt, with 2 mols. H_2O, is less soluble in water, and crystallises in crusts of small needles; the *silver* and *cobalt* salts are also described.

Dimetanitroparatolylacetic acid, $C_6H_2Me(NO_2)_2{\cdot}CH_2{\cdot}COOH$

$$[CH_2{\cdot}COOH : NO_2 : Me : NO_2 = 1 : 3 : 4 : 5],$$

is formed when paratolylacetic acid is added in small quantities to five times its weight of a mixture of fuming nitric acid with twice its weight of pure sulphuric acid cooled below 0° in a freezing mixture. It crystallises from water or dilute alcohol in colourless, silky needles, melts at 158° (uncorr.), and is less soluble than the nitro-acid in boiling water, but equally soluble in alcohol, ether, &c. On oxidation with the calculated quantity of potassium permanganate, it yields dimetanitroparatoluic acid. The *sodium* salt, with 5 mols. H_2O, crystallises in colourless, flat needles, and is less soluble in hot or cold water than the sodium salt of the nitro-acid; the *calcium* salt crystallises in anhydrous, sparingly soluble, colourless prisms.

Paratolylbromacetic acid, $C_6H_4Me{\cdot}CHBr{\cdot}COOH$, is obtained when paratolylacetic acid, dissolved in a small quantity of acetic acid, is mixed with the calculated quantity of bromine and 30 times its weight of water and exposed to direct sunlight for some days. It crystallises from water in colourless, short needles, and melts at 125° (uncorr.); it is very sparingly soluble in cold water, but readily in alcohol, ether, chloroform, benzene, and acetic acid. The *barium* salt, with 3 mols. H_2O, crystallises in small, colourless, lustrous scales, and is easily soluble in hot water, but only sparingly in the cold.

Paratolylacetamide crystallises from concentrated aqueous solutions in nacreous scales, from dilute solutions in long, white needles, and melts at 185°. W. P. W.

Bismuth Salicylate. By H. CAUSSE (*Compt. rend.*, **112**, 1220—1223).—The preparation of bismuth salicylate is a matter of some difficulty, because water decomposes the bismuth salts, whilst acids decompose the salicylates. Ammonium salts, however, especially ammonium chloride, tend to prevent the decomposition of the bismuth salts by water, although they have practically no solvent action on the basic bismuth salts themselves.

Basic bismuth nitrate, 100 grams, is dissolved in concentrated hydrochloric acid with the aid of heat, and the solution is poured into 1000 c.c. of a saturated solution of ammonium chloride. The free acid is neutralised either by adding more basic nitrate or by adding a solution of ammonia in ammonium chloride solution until a slight permanent precipitate remains after vigorous agitation. A solution of 120 grams of sodium salicylate in 500 c.c. of saturated ammonium chloride solution is then added, and in a short time the liquid is filled with a bulky, crystalline precipitate of bismuth salicylate, which is drained and washed with water until all ammonium chloride is removed. The dried product has the composition $Bi(C_7H_5O_3)_3 + 4H_2O$, resembles quinine in appearance, is insoluble in water, and is decomposed by acids. It is not affected by cold water, but is decomposed by boiling water and also by absolute alcohol, with separation of bismuth oxide. When heated at 50°, salicylic acid slowly sublimes, and at 100° decomposition is complete. C. H. B.

Catecholcarboxylic Acids. By R. SCHMITT and H. HÄHLE (*J. pr. Chem.* [2], **44**, 1—5).—The introduction of one carboxyl radicle into catechol and resorcinol can be effected, as is known, by heating these phenols with ammonium carbonate or potassium hydrogen carbonate, but further substitution can only be brought about by heating the monocarboxylates with carbonic anhydride under considerable pressure. When the dry sodium salt of catechol is exposed to the action of compressed carbonic anhydride at the ordinary temperature, 2 molecular proportions of the gas enter into reaction with the formation of sodium orthophenylenecarboxylate, which, by prolonged heating in an autoclave with compressed carbonic anhydride at 120—140° yields sodium catecholcarboxylate, and if the heating is continued at 210° for eight hours, sodium catecholdicarboxylate is formed, mixtures of the two acids being obtained at intermediate temperatures. As the monocarboxylic acid dissolves readily in water, in which the dicarboxylic acid is insoluble, the two compounds can be easily separated. The former proves to be identical with Miller's orthodihydroxybenzoic acid (*Annalen*, **220**, 116).

Catecholdicarboxylic acid, $C_6H_2(OH)_2(COOH)_2$, crystallises from water in slender, colourless needles, with 1 mol. H_2O, and from alcohol in anhydrous, yellow scales; it melts at 290° with evolution of carbonic anhydride, does not volatilise with steam, and is only sparingly soluble in hot water and chloroform, but more so in alcohol and ether. The solutions exhibit a deep-blue fluorescence, and the aqueous solution is coloured deep indigo-blue by ferric chloride, and yellow by lead acetate. The *sodium* salt, $C_6H_2(OH)_2(COONa)_2 + 2H_2O$, crystallises in concentrically grouped prisms, which show a marked blue fluorescence, and are readily soluble in water but insoluble in alcohol; the *barium* salt forms tufts of sparingly soluble prisms; the *silver* and *lead* salts are also described. The *dimethyl* salt, $C_6H_2(OH)_2(COOMe)_2$, crystallises in slender, colourless needles, melts at 145°, is insoluble in water but volatile with steam, and dissolves readily in alcohol and ether, forming fluorescent solutions; the *diethyl* salt crystallises in colourless, prismatic tables, melts at 89—90°, and resembles the dimethyl salt in solubility and fluorescence.

Of the sodium salts of the three dihydroxybenzenes, that of catechol is the most sensitive to the action of air. When prepared in an indifferent atmosphere, it is a white powder, which dissolves readily in water and can be rendered anhydrous without difficulty, since it may be heated at 220° in a current of hydrogen without decomposition.

W. P. W.

Preparation of Phenoldicarboxylic Acids. By H. HÄHLE (*J. pr. Chem.* [2], **44**, 5—14).—It has been shown that unsymmetrical hydroxyisophthalic acid, free from the consecutive acid, is obtained when either basic sodium salicylate or a mixture of that salt with basic potassium salicylate is heated in a current of carbonic anhydride at 300—400°, the entering carboxyl radicle assuming the para-position relatively to the hydroxyl (Ost, this Journ., 1877, ii, 485). The consecutive acid can, however, be prepared if the basic sodium salt of methyl salicylate, in which an alkyl radicle instead of a metal is substituted for the carboxylic hydrogen, is heated with carbonic anhydride under considerable pressure, and in like manner dicarboxylic acids containing carboxyl in the ortho-position relatively to the hydroxyl may be obtained from meta- and para-hydroxybenzoic acids.

The basic sodium salt of methyl salicylate is formed when oil of wintergreen, dissolved in an equal quantity of 96 per cent. alcohol, and cooled at 0°, is treated with the requisite quantity of titrated aqueous soda, also mixed with an equal quantity of alcohol. After stirring for a short time, the salt very rapidly separates in lustrous, thin, white scales, and can be obtained perfectly dry by thinning the almost solid mass with alcohol and ether, filtering, pressing, and heating at 140° in a vacuum.

Methyl hydrogen hydroxyisophthalate [$COOMe:OH:COOH = 1:2:3$] is obtained when the perfectly dry basic sodium salt of methyl salicylate is heated with excess of carbonic anhydride in an autoclave at 150° for about 24 hours. The amount of carbonic anhydride taken up in the reaction did not exceed that corresponding with a half molecular proportion under the various conditions employed. The product is extracted with ether to remove the methyl salicylate and methyl orthomethoxybenzoate formed in the reaction, and subsequently heated on a water-bath with dilute hydrochloric acid. The solution is then rendered slightly alkaline with aqueous ammonium carbonate, steam-distilled to remove any methyl salicylate, acidified, extracted with ether, and the ethereal solution repeatedly precipitated by ammonia. The salt crystallises in characteristic stellate groups of flat needles, which, when powdered, become strongly electrified. It melts at 135°, and also when heated under water; it dissolves readily in alcohol or ether, sparingly in cold but readily in hot water, and in aqueous solution shows a marked blue fluorescence. With ferric chloride in aqueous solution, it gives a carmine coloration. The *sodium* salt, $COOMe\cdot C_6H_3(OH)\cdot COONa + H_2O$, crystallises in slender, colourless, concentrically-grouped needles, and dissolves readily in water, forming a solution which exhibits a beautiful blue fluorescence. On hydrolysis, it yields consecutive hydroxyisophthalic acid. It is to be noted that Ost's unsymmetrical hydroxyisophthalic acid is always present in the product, although only in very small quantity; the acids can be readily separated by means of the barium salts, since that of the consecutive acid is only sparingly soluble in water, whilst that of the unsymmetrical acid is easily soluble.

When the reaction between the basic sodium salt of methyl salicylate and carbonic anhydride is conducted at 170° or above, the product consists of a mixture of the sodium salt of consecutive hydroxyisophthalic acid with methyl orthomethoxybenzoate owing to the occurrence of the reaction $COOMe\cdot C_6H_3(OH)\cdot COONa + ONa\cdot C_6H_4\cdot COOMe = OH\cdot C_6H_3(COONa)_2 + OMe\cdot C_6H_4\cdot COOMe$. This accounts for the presence of methyl orthomethoxybenzoate in the product formed at lower temperatures, and for the fact that the amount of carbonic anhydride taken up is only one-half that which was anticipated.

Ethyl salicylate, when treated in like manner, yields consecutive isophthalic acid, but the phenyl salt cannot be employed, since it decomposes into phenol and the basic sodium salt of ethyl salicylate on treatment with sodium ethoxide in alcoholic solution.

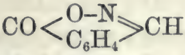
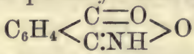
Sodium ethyl hydroxyisophthalate [COOEt : COONa : OH = 1 : 3 : 4] is formed quantitatively when the perfectly dry basic sodium salt of ethyl parahydroxybenzoate is heated with carbonic anhydride under pressure at 160—170°, one molecular proportion of the gas entering into reaction. It crystallises in beautiful, colourless prisms, and, on treatment with hydrochloric acid, is converted into *ethyl hydrogen hydroxyisophthalate*, which crystallises from alcohol in colourless, monoclinic scales, melts at 194—195°, and, on hydrolysis, yields unsymmetrical hydroxyisophthalic acid. The basic sodium salt of methylparahydroxybenzoate under like conditions also yields the unsymmetrical acid.

When the basic sodium salt of ethylmetahydroxybenzoate is heated with carbonic anhydride under pressure at 170°, and after the operation has continued some time, the material, which tends to agglomerate, is powdered and again submitted to the action of the gas, one molecular proportion of the anhydride is taken up with the production of sodium ethyl hydroxyterephthalate, from which hydroxyterephthalic acid can be obtained by hydrolysis. As the chloroterephthalic acid, which can easily be prepared from this acid, readily undergoes reduction with elimination of the chlorine, this would seem to afford the best method of preparing terephthalic acid.

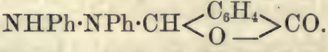
The phenyl salts of the hydroxyisophthalic acids are described since they serve as an additional means of identification. *Phenyl* 1 : 2 : 3-*hydroxyisophthalate* crystallises from alcohol in colourless prisms, and melts at 99°. *Phenyl ethyl* 1 : 3 : 4-*hydroxyisophthalate* [COOEt : COOPh : OH = 1 : 3 : 4], obtained by heating the ethyl hydrogen salt with phenol and phosphorus oxychloride, crystallises from alcohol in colourless needles, and melts at 64—65°.

W. P. W.

Phthalaldehydic Acid. By O. ALLENDORFF (*Ber.*, **24**, 2346—2354).—Liebermann (Abstr., 1887, 46) obtained hemipinimide by boiling an alcoholic solution of opianic acid with hydroxylamine hydrochloride, but he afterwards found (*ibid.*, 258) that when the reaction took place at the ordinary temperature, opianoximic anhydride was produced, the latter undergoing an intramolecular change when heated with formation of hemipinimide. Racine (*Annalen*, **239**, 81) obtained benzaldoximorthocarboxylic acid by mixing aqueous solutions of phthaldehydic acid and hydroxylamine hydrochloride, and this acid yielded the anhydride, phthalimide, on heating. The oximic acid is therefore wanting in the hemipinic series, and the corresponding anhydride in the phthalyl series.

Benzaldoximorthocarboxylic anhydride,  $CO<\genfrac{}{}{0pt}{}{O-N}{C_6H_4}>CH$, separates in white crystals when phthalaldehydic acid (4 grams) is dissolved in 80 per cent. alcohol (12 grams) and hydroxylamine hydrochloride (2·2 grams) added with frequent shaking. It slowly dissolves with decomposition in sodium carbonate solution, and on fusion it behaves like opianoximic anhydride (*loc. cit.*) thus :—When quickly heated to 120°, the temperature suddenly rises to 215° with formation of the isomeric phthalimide; whilst if carefully heated in a capillary tube, it melts at 187°, resolidifies, and then melts again at 225—228°. This is explained as follows: the benzaldoximecarboxylic anhydride is converted at 120° into an isomeride melting at 187°, and this, later on, undergoes intramolecular change into phthalimide, as the temperature is raised. The intermediate compound (m. p. 187°) is obtained when benzaldoximorthocarboxylic anhydride is heated in an oil-bath at 145°, and the product extracted with boiling benzene and crystallised from aqueous acetone. It is distinguished from benzaldoximorthocarboxylic anhydride by its insolubility in benzene, and from phthalimide by its more ready solubility in cold sodium carbonate solution. It is identical with the compound obtained by Kuhara (Abstr., 1881, 1039) from phthalyl chloride and ammonia, and has one of the two formulæ  $C_6H_4<\genfrac{}{}{0pt}{}{C{=}O}{C{:}NH}>O$ or $CN{\cdot}C_6H_4{\cdot}COOH$; the second, orthocyanobenzoic acid, being the more probable from the solubility of the compound in sodium carbonate solution. Phthalimide is obtained direct when an alcoholic solution of phthalaldehydic acid and hydroxylamine hydrochloride is boiled in a reflux apparatus for some time. An attempt to prepare opianoximic acid by the action of hydroxylamine hydrochloride on opianic acid in aqueous solution led to a negative result, the anhydride alone being formed.

Diphenylhydrazonephthalaldehydic acid, $C_6H_4(CH{:}N{\cdot}NPh_2){\cdot}COOH$, is prepared by adding a hot concentrated aqueous solution of asymmetrical diphenylhydrazine hydrochloride (1 mol.) to one of phthalaldehydic acid and sodium acetate in molecular proportion, together with a trace of hydrochloric acid; on boiling the mixture for a short time, a green, resinous precipitate separates, which is purified by crystallisation, first from a small quantity of glacial acetic acid, and then from benzene. It forms lustrous, yellow, truncated prisms, melts at 187°, and is readily soluble in ether, alcohol, acetone, chloroform, and hot benzene, but insoluble in water and light petroleum. The *calcium salt* is a yellow precipitate. The acid, and not the ethyl salt, is formed by the action of diphenylhydrazine hydrochloride on ethyl phthalaldehydate.

Phthalidylhydrazobenzene, $C_{20}H_{16}N_2O_2$, is formed when hot alcoholic solutions containing hydrazobenzene and phthalaldehydic acid, in molecular proportion, are mixed; the white crystals which separate are obtained as lustrous needles on recrystallisation from absolute alcohol; it darkens at 150°, melts at 202—203°, and is readily soluble in benzene, acetone, and chloroform, less so in alcohol and ether, and insoluble in water and light petroleum. It is not a carboxylic acid, does not contain an aldehyde group, and has probably a constitution analogous to Bistrzycki's opianylhydrazobenzene (Abstr., 1888, 1209), thus:  $NHPh{\cdot}NPh{\cdot}CH<\genfrac{}{}{0pt}{}{C_6H_4}{O\text{—}}>CO$.

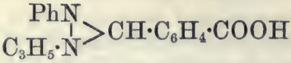
Benzidylphthalaldehydic acid, $C_{12}H_8(N{:}CH{\cdot}C_6H_4{\cdot}COOH)_2$, is obtained when aqueous solutions of phthaldehydic acid (2 mols.) and benzidine (1 mol.) are boiled together for a short time; it separates as a white, pulverulent precipitate, and may be purified by boiling with absolute alcohol. It is insoluble in the ordinary solvents, but dissolves in boiling nitrobenzene and in cold sodium carbonate solution; it also dissolves in concentrated sulphuric acid with a yellow coloration, which soon changes to brownish-red. When the *calcium salt* is boiled with water, benzidine is eliminated.

Methylphenylhydrazonephthalaldehydic acid,

$$NMePh\cdot N{:}CH\cdot C_6H_4\cdot COOH,$$

is produced when hot concentrated alcoholic solutions containing phthalaldehydic acid and methylphenylhydrazine, in molecular proportion, are mixed and boiled together for a short time. It forms bright-yellow crystals, melts at 167°, and is easily soluble in alcohol, benzene, chloroform, ether, and acetone, but only sparingly in light petroleum, and is insoluble in water.

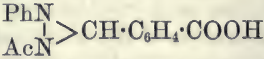
Allylphenylhydrazonephthalaldehydic acid,



$\begin{array}{c}PhN\\ |\\ C_3H_5\cdot N\end{array}\!>CH\cdot C_6H_4\cdot COOH$,

is obtained by mixing hot concentrated solutions of symmetrical allylphenylhydrazine and phthalaldehydic acid in molecular proportion, and boiling for a short time. It crystallises from alcohol in lustrous, yellow prisms, melts at 160°, and is easily soluble in alcohol, benzene, acetone, chloroform, and dilute solutions of alkali carbonates, sparingly in light petroleum, and is insoluble in water; it dissolves in concentrated sulphuric acid with a red colour.

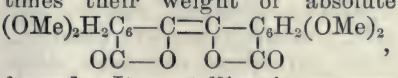
Acetylphenylhydrazonephthalaldehydic acid,



$\begin{array}{c}PhN\\ |\\ AcN\end{array}\!>CH\cdot C_6H_4\cdot COOH$, is

formed by boiling together phthalaldehydic acid and acetylphenylhydrazine in molecular proportion. It crystallises from dilute alcohol in small, granular crystals, melts at 191°, and is soluble in alcohol, chloroform, and hot benzene, fairly so in hot water, and almost insoluble in ether and light petroleum; it dissolves slowly in cold solutions of alkali carbonates. A. R. L.

Action of Potassium Cyanide on Ethyl Opianate. By G. GOLDSCHMIEDT and L. EGGER (*Monatsh.*, **12**, 49—80).—In many of its reactions, opianic acid behaves as an aldehydo-orthocarboxylic acid, $COH\cdot C_6H_2(OMe)_2\cdot COOH$; whilst in others, it resembles the isomeric anhydride (Liebermann, Abstr., 1886, 550, and 1887, 45). The authors consequently expected that the compound, when treated with potassium cyanide, would not behave in the same way as benzaldehyde and anisaldehyde, which give rise to benzoïn and anisoïn respectively. This supposition proves to be correct, for when equal weights of perfectly dry ethyl opianate and potassium cyanide are intimately mixed and heated in a reflux apparatus for one hour with 10—12 times their weight of absolute alcohol, *tetramethoxydiphthalyl*,



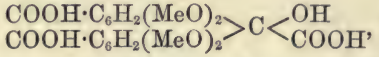
$\begin{array}{l}(OMe)_2H_2C_6-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}_6H_2(OMe)_2\\ \qquad\quad OC-O\quad O-CO\end{array}$, a very insoluble compound, is

formed. It crystallises in masses of brilliant, yellow, slender needles, having a beautiful, green fluorescence, which is also shown in chloroform or in acetic acid solution, or, best of all, when the substance is shaken with water. It does not change when heated to 300°; but above this, it commences to blacken, and only melts when the temperature is further considerably raised. It is almost insoluble in ordinary solvents; may be sublimed with partial decomposition. It is not changed by cold concentrated potash, but dissolves when warmed with it, forming a yellow solution. A small quantity of the substance imparts an orange-red colour and a strong, yellow fluorescence to concentrated sulphuric acid, and the solution thus obtained becomes claret-coloured on heating, whilst the addition of a small quantity of nitric acid turns it green, indigo-blue, violet, and fiery-red successively.

Tetrahydroxydiphthalyl, $C_{16}H_4O_4(OH)_4$, obtained by the action of hydriodic acid on the tetramethoxydiphthalyl, is a greenish-grey powder, which commences to blacken at 300°, without previously melting. It is almost insoluble in alcohol, benzene, carbon bisulphide, and xylene, and only sparingly soluble in acetone, amyl alcohol, and ethyl acetate, crystallising from the last-named solvent in yellow, microscopic needles. With dilute ammonia, it gives an intense dark-green coloration, which becomes of a beautiful lilac on the addition of hydrochloric acid.

Tetramethoxydiphthalyldicarboxylic acid, $C_2O_2[C_6H_2(OMe)_2\cdot COOH]_2$ $[COOH : (OMe)_2 : CO = 1 : 4 : 5 : 6]$, is obtained when a mixture of tetramethoxydiphthalyl (2 grams) and potash (1 gram) in alcohol (30 grams) is heated in a reflux apparatus. The product of the reaction is a reddish-yellow liquid, which, on dilution with water, evaporation of the alcohol, and addition of hydrochloric acid, furnishes the acid in the form of white, microscopic, rhombic scales. It commences to decompose at 220° and melts at 270°, dissolves readily in alkalis, giving a yellow solution, and reduces ammoniacal silver nitrate when boiled with it. The acid is almost insoluble in water, dissolves readily in acetone, but is best recrystallised from alcohol; the *barium* salt, $C_{20}H_{16}O_{10}Ba + 3H_2O$, forms shining, yellow crystals; the *dihydrazone* is not characteristic. On heating the acid in a flask placed in an oil-bath at 250°, a sublimate of hemipinic acid, melting at 166—167°, is obtained, whilst the residue in the flask consists of tetramethoxydiphthalyl. When the acid (1 gram) is fused with solid potash (5 grams), a substance which is most probably methylnorhemipinic acid (compare Wegscheider, *Monatsh.*, **3**, 376) is obtained.

Tetramethylbenzhydroletricarboxylic acid,

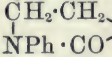


$$\begin{array}{l}COOH\cdot C_6H_2(MeO)_2\\ COOH\cdot C_6H_2(MeO)_2\end{array}\!>C<\!\begin{array}{l}OH\\ COOH,\end{array}$$

is obtained on heating tetramethoxydiphthalyl (2 grams) with a large excess of potash (10 grams) in absolute alcohol (100 grams). It melts at 140°, is soluble in water, alcohol, ether, and acetone, and gives, with concentrated sulphuric acid, a beautiful scarlet coloration. The *barium* salt, $(C_{20}H_{17}O_{11})_2Ba_3 + 5H_2O$, crystallises in slender, silky needles, and is readily soluble in water.

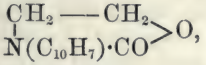
When the alcoholic filtrate obtained after separation of the tetramethoxydiphthalyl from the products of the reaction of potassium cyanide and ethyl opianate is evaporated to a syrupy consistence and allowed to remain over night, a considerable quantity of ethyl hemipinate (m. p. 71°) crystallises out. From the mother liquor, by cautious addition of hydrochloric acid, a brownish resin is precipitated, and this, on evaporation of its alcoholic solution, gives colourless crystals of *tetramethoxydihydrodiphthalyl*, $C_{20}H_{18}O_8$, melting at 204°. On evaporating the solution from which the resin has separated, an uncrystallisable syrup is obtained having the properties of an acid.

Ethyl hemipinate and tetramethoxydihydrodiphthalyl are formed when an alcoholic solution of potassium cyanide is warmed with tetramethoxydiphthalyl; they must, therefore, be regarded as secondary products in the action of potassium cyanide on ethyl opianate. G. T. M.

Action of Carbonic Chloride on Glycol Chlorhydrins. By P. OTTO (*J. pr. Chem.* [2], **44**, 15—23).—By acting on glycol chlorhydrin with carbonic chloride, Nemirowsky (Abstr., 1885, 741) obtained ethyl chlorethylchlorocarbonate, which, by the action of aniline and treatment of the resulting ethyl chlorethylphenylcarbamate with aqueous caustic potash, gave the compound  $\left.\begin{array}{l}CH_2\cdot CH_2\\ NPh\cdot CO\end{array}\right>O$. The author finds that if very concentrated aqueous potash is employed, an oil is obtained, which, unlike the anhydride, is soluble in ether and has basic properties. On distillation, the greater part, consisting of hydroxyethylaniline, passes over at 280—285°, whilst the residue in the retort crystallises from alcohol in needles, melts at 154°, and is identical with Hofmann's diethylenediphenyldiamine.

Hydroxyethylaniline is best prepared by boiling glycol chlorhydrin (10 grams) with recently distilled aniline (22 grams) in a reflux apparatus for 16 minutes, rendering the product alkaline, and extracting with ether. The yield amounts to 70 per cent. of the theoretical. When a mixture of hydroxyethylaniline with liquid carbonic chloride is kept in a tube for about five hours, a crystalline magma consisting of Nemirowsky's anhydride is obtained. This compound is also formed, together with hydroxyethylaniline hydrochloride, when a current of carbonic chloride is passed into an ethereal solution of hydroxyethylaniline. The anhydride is, moreover, obtained when methylhydroxyethylaniline is treated with carbonic chloride, methyl chloride being eliminated in the condensation.

Ethyl chlorethyl-α-naphthylcarbamate, $CH_2Cl\cdot CH_2\cdot O\cdot CO\cdot NH\cdot C_{10}H_7$, prepared by treating α-naphthylamine with ethyl chlorethylchlorocarbonate under water, crystallises from alcohol in long, matted needles, melts at 100—101°, and is readily soluble in alcohol and ether, but practically insoluble in water. The β-compound forms lustrous scales, melts at 98°, and dissolves readily in alcohol and ether. On treatment with aqueous caustic potash (1 : 2), both substances yield the corresponding anhydrides. The α-compound,



$$\left.\begin{array}{l}CH_2 — CH_2\\ N(C_{10}H_7)\cdot CO\end{array}\right>O,$$

crystallises in scales, melts at 125°, and is insoluble in ether, but readily soluble in hot alcohol; the β-derivative crystallises in prisms, melts at 189°, and is insoluble in ether, sparingly soluble in hot alcohol. With a saturated caustic potash solution, however, analogues of hydroxyethylaniline are obtained, which dissolve in ether, and on evaporation of the solutions are obtained in the crystalline form. *Hydroxyethyl-α-naphthylamine*, $OH·CH_2·CH_2·NH·C_{10}H_7$, crystallises in needles, melts at 52°, and is very soluble in alcohol and ether. The solutions, on evaporation, leave oily drops, which slowly crystallise with formation of blue needles. The β-compound crystallises in scales, melts at 51°, and is extremely soluble in alcohol and ether. Its *hydrochloride* separates from hot water in lustrous scales, and, unlike the hydrochloride of the α-compound, does not reduce silver solutions.

Ethyl dichlorisopropylchlorocarbonate, $CH(CH_2Cl)_2·O·COCl$, is formed when α-dichlorhydrin is heated with liquid carbonic chloride at 170° for about 24 hours. It boils at 185—187°, and on treatment with aniline and α- and β-naphthylamine, yields a series of compounds which dissolve readily in alcohol and ether, and are converted into the corresponding anhydrides by the action of aqueous caustic potash (1 : 2). *Ethyl dichlorisopropylcarbamate* crystallises in large, seemingly rhombic forms melting at 80°, *ethyl dichlorisopropylphenylcarbamate* in large, seemingly rhombic forms melting at 73°, *ethyl dichlorisopropyl-α-naphthylcarbamate* in lustrous, white needles melting at 115°, whilst *ethyl dichlorisopropyl-β-naphthylcarbamate* forms scales melting at 101°. The anhydrides are readily soluble in alcohol, but insoluble in ether; the anhydride obtained from the phenylcarbamate crystallises in long needles melting at 103°, that from the α-naphthylcarbamate in scales which melt at 118°, and that from the β-naphthylcarbamate in needles melting at 107°.

Ethyl β-dichloropropylchlorocarbonate is obtained when β-dichlorhydrin cooled in ice-cold water is treated with a small excess of carbonic chloride, and the reaction allowed to continue during about six hours, until hydrogen chloride is no longer evolved; it boils at 185—187°, and has the odour of ethyl chlorocarbonate. *Ethyl αβ-dichloropropylcarbamate* crystallises in large, rhombic forms melting at 75°, *ethyl αβ-dichloropropylphenylcarbamate* in prisms melting at 73—74°, *ethyl αβ-dichloropropyl-α-naphthylcarbamate* in lustrous needles which melt at 93°; and *ethyl αβ-dichloropropyl-β-naphthylcarbamate* in scales melting at 99°. These compounds do not react either with dilute (1 : 2) or concentrated aqueous potash. W. P. W.

Paraxylenedisulphonic Acid. By J. H. Holmes (*Amer. Chem. J.*, **13**, 371—384).—*Xylenedisulphonic chloride*, $C_6H_2Me(SO_2Cl)_2$, was prepared as follows:—Paraxylene (35 grams) was added, with constant shaking, to twice its volume of fuming sulphuric acid diluted with a small quantity of ordinary acid, and the mixture first cooled, but finally warmed. The solution was diluted (4 or 5 litres), neutralised with chalk, filtered, evaporated (2 litres), sodium carbonate added, again filtered, and evaporated to dryness. The sodium xylenesulphonate thus obtained was treated with phosphorus pentachloride (equal weight), the product heated for some time on the water-bath, and much water added, when xylenesulphonic chloride separated as an oily liquid, which did not entirely solidify in a freezing mixture. This chloride was treated with fuming sulphuric acid as long as a drop of the mixture gave a turbidity when dropped into water; the acids were neutralised with chalk, the sodium salt obtained as above, and treated with twice its weight of phosphorus pentachloride. After evaporating off the phosphorus oxychloride, the xylenedisulphonic chloride was separated by pouring the mixture into several litres of water; it crystallises from light petroleum in white, radiating tufts, and melts at 72—74°. It dissolves easily in cold alcohol, from which, however, it cannot be again obtained; it is soluble also in other organic solvents, but will not crystallise from them.

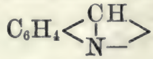
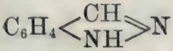
Xylenedisulphonic acid, $C_6H_2Me_2(SO_3H)_2$, is obtained from the chloride by boiling it with water in a reflux apparatus, evaporating the solution on the water-bath several times, until no more hydrochloric acid is given off, and decolorising with animal charcoal; it crystallises in needles, which are very soluble in water. The *barium*, *calcium* (with 4 mols. H_2O), *lead* (with 3 mols. H_2O), *magnesium* (with 7 mols. H_2O), and *silver* (with 1 mol. H_2O) salts are described; they are very hygroscopic. The authors found that a second preparation of the acid would not crystallise, and gave an amorphous calcium salt; the last three salts mentioned above were made from this preparation. The *amide*, $C_6H_2Me_2(SO_2NH_2)_2$, made by the action of ammonia on the chloride, crystallises from water in microscopic, thin, tabular plates, and from a hot solution in dilute alcohol in very small, satiny crystals, which do not settle, even on long standing, It melts with partial decomposition at 294—295°, and dissolves readily in acetone and pyridine, but only slightly in water, glacial acetic acid, chloroform, or ether. The amide obtained from the uncrystallisable acid was mostly amorphous.

Disulphamineparatoluic acid, $C_6H_2Me(SO_2NH_2)_2\cdot COOH + H_2O$, is obtained by oxidising the above amide with alkaline potassium permanganate; it forms ill-defined crystals which melt about 272°; it burns on platinum foil, leaving no residue. The *potassium* (with 2 mols. H_2O), *barium* (with $2\frac{1}{2}$ mols. H_2O), *calcium*, *lead* (with 3 mols. H_2O), and *silver* (with 2 mols. H_2O) salts are described.

The amorphous amide referred to above gave a small quantity of another oxidation product when treated with alkaline permanganate; this formed crystals melting about 274°, but was not further investigated.

The evidence obtained in this investigation is insufficient to settle the orientation of the sulphonic acid groups in this disulphonic acid.

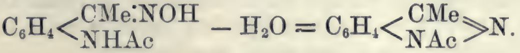
A. G. B.

New Synthesis of Isindazole Derivatives. By K. Auwers and F. v. Meyenburg (*Ber.*, **24**, 2370—2388).—According to the investigations of E. Fischer and his pupils, indazole and isindazole compounds are derived from the hypothetical substances  $C_6H_4{<}\begin{matrix}CH\\|\\N—\end{matrix}{>}NH_2$ and  $C_6H_4{<}\begin{matrix}CH\\NH\end{matrix}{\gg}N$ respectively; the evidence is, on the one hand, the formation of 3′-methylindazole from acetophenoneorthohydrazinesulphonic acid, and on the other hand the fact that, with the single exception of the synthesis of nitrophenylisindazolecarboxylic acid (V. Meyer, Abstr., 1889, 516), all the known derivatives of isindazole have been obtained from alkylated amido-derivatives of benzene. Although the formation of isindazole derivatives is *a priori* to be expected when the oximes of aromatic orthamidoketones are treated with dehydrating agents, that of indazole derivatives is not impossible; indeed, on glancing at the above formulæ, it is seen that these only represent desmotropic forms of the same compound, and that true isomerism can only occur when the imidic hydrogen is substituted.

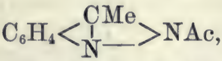
Orthamidacetophenone oxime, $NH_2{\cdot}C_6H_4{\cdot}CMe{:}NOH$, is obtained when orthamidacetophenone (1 mol.), hydroxylamine hydrochloride (3 mols.), and potassium hydroxide (8—9 mols.) are digested in alcoholic solution on the water-bath for half an hour. The solution is filtered from potassium chloride, the greater portion of the alcohol evaporated off, and water added; the bulk of the oxime then separates as a white, crystalline mass, the remaining portion being precipitated by a stream of carbonic anhydride. The same oxime is slowly formed by the action of an alkaline solution of hydroxylamine on orthamidacetophenone at the ordinary temperature, or when the ketone is heated with an alcoholic solution of hydroxylamine hydrochloride (3 mols.) at 100—160°; at the higher temperature, however, much of the product resinifies. The compound is easily soluble in boiling water, crystallises therefrom in small, delicate, felted needles, and melts at 109°; it is also readily soluble in alcohol, ether, and benzene, but only sparingly in light petroleum; water containing a few drops of hydrochloric acid dissolves it readily, whilst it is less soluble in concentrated hydrochloric acid. It is very stable when heated, distils with slight decomposition only, and sublimes at the temperature of the water-bath. The *hydrochloride* separates from water in clusters of long, delicate needles. The *diacetyl derivative*, $NHAc{\cdot}C_6H_4{\cdot}CMe{:}NOAc$, is prepared by pouring over the oxime twice its weight of acetic anhydride, when it dissolves with development of heat, the new compound separating after a time in iridescent plates; it is completely precipitated on adding water. After crystallisation from 30 per cent. alcohol, it melts at 127°; it is hydrolysed when left in contact with aqueous sodium hydroxide for 1—2 days.

1′ : 3′-*Acetylmethylisindazole*, $C_{10}H_{10}N_2O$, is best prepared by dissolving the oxime described above (1 part) in a mixture of glacial acetic acid (8 parts) and acetic anhydride (2 parts), saturating the solution, cooled by water, with hydrogen chloride, and allowing it to remain at the ordinary temperature for four days; the yellowish-red liquid is then concentrated on the water-bath to a syrup, and saturated with sodium carbonate. The precipitate is collected and spread on a porous tile; a further quantity may be extracted from the mother liquor by ether. It crystallises from a small quantity of boiling water in delicate, silky, colourless needles, melts at 103°, is readily soluble in all organic solvents, with the exception of light petroleum, but only sparingly in aqueous alkalis. The compound closely resembles E. Fischer's methylindazole, and has the same sweet taste; it yields a compound with mercuric chloride, crystallising from boiling water in needles. One of its chief characteristics is a tendency to separate out in a delicate, arborescent form, when its solution in a volatile solvent is left to evaporate. In the dry condition it slowly acquires a yellow colour, but when moist it rapidly becomes of an intense red. Its aqueous solution has a strong, green fluorescence, whilst its solution in an alkali resembles an alcoholic solution of chlorophyll. Attempts to prepare isindazole from orthamidobenzophenone oxime and hydrochloric acid led to negative results.

Acetylorthamidacetophenone oxime, $C_{10}H_{12}N_2O_2$, is obtained when a dilute alcoholic solution of acetylorthamidacetophenone (Baeyer and Blöm, Abstr., 1883, 198) (2 grams), hydroxylamine hydrochloride (3 grams), and caustic alkali (2 grams) is heated on the water-bath for 4—5 hours. After purification, it separates from boiling water in colourless, flat needles, and from benzene in lustrous prisms; it melts at 149—150°. When the oxime is treated with a mixture of glacial acetic acid and acetic anhydride, the above-described 1′ : 3′-acetylmethylisindazole is formed, thus:—



$$C_6H_4\lt\begin{matrix}CMe{:}NOH\\ NHAc\end{matrix} - H_2O = C_6H_4\lt\begin{matrix}CMe\\ NAc\end{matrix}\gt N.$$

2′ : 3′-*Acetylmethylindazole*,  $C_6H_4\lt\begin{matrix}CMe\\ |\\ N\end{matrix}\gt NAc$, is prepared by acetylating E. Fischer's methylindazole (m. p. 113°; *Annalen*, **227**, 316); it crystallises from 30 per cent. alcohol in thin plates or long needles, and melts at 72°. When the acetylmethylindazole is heated with aqueous sodium hydroxide for 1—2 hours on the water-bath, methylindazole (m. p. 113°) is obtained; whereas the acetylmethylisindazole, under similar conditions, yields orthamidacetophenone oxime.

Orthamidacetophenone hydrazone, $C_{14}H_{15}N_3$, is obtained in nearly theoretical yield, when orthamidacetophenone is digested in alcoholic solution with an excess of phenylhydrazine acetate for 1—2 hours on the water-bath. It is precipitated by sodium carbonate, and purified by crystallisation from a small quantity of boiling alcohol, with the addition of animal charcoal; it separates in small, delicate needles, melts at 108°, and is readily soluble in boiling water, as well as in most organic solvents, with the exception of light petroleum. The *oxime*, $C_{13}H_{12}N_2O$, is obtained when orthamidobenzophenone, prepared by Geigy and König's method (Abstr., 1885, 1236), is heated with hydroxylamine and an excess of alkali in dilute alcoholic solution for 4—5 hours on the water-bath. After filtering and driving off most of the alcohol, it is precipitated by a stream of carbonic anhydride, and crystallised from dilute alcohol. It forms small, delicate needles or four-sided plates, melts at 156°, and is readily soluble in most solvents, except cold water and benzene. The yield is only 50—60 per cent. of the theoretical, and is not improved by conducting the experiment at the ordinary temperature; as the melting point only becomes constant after repeated crystallisation, an isomeride (see below) is, perhaps, simultaneously formed. The *diacetyl derivative*, $C_{17}H_{16}N_2O_3$, melts at 218°, and is sparingly soluble in most solvents; dilute sodium hydroxide decomposes it into the oxime.

1′ : 3′-*Acetylphenylisindazole*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CPh}{NAc}{>}N$, is obtained when the amidobenzophenone is allowed to remain for 10 days with a mixture of glacial acetic acid and acetic anhydride. The solution is evaporated, aqueous sodium carbonate added, and the crude substance repeatedly crystallised from dilute alcohol. The compound has all the properties of an indazole derivative; it dissolves readily in most solvents and in hot water, crystallises in small, lustrous plates or needles, and melts at 185°. When digested with dilute sodium hydroxide for 1—2 hours on the water-bath, a compound is obtained having the composition of an *amidobenzophenone oxime*, which melts at 123—125°, and yields a *diacetyl derivative*, melting at 218°. The existence of a single amidacetophenone oxime and of two amidobenzophenone oximes is in agreement with the observations of Hantzsch (this vol., p. 36).

Acetylorthamidobenzophenone, $C_{15}H_{13}NO_2$, is formed when orthamidobenzophenone is gently heated with acetic anhydride. It crystallises from dilute alcohol in scales and thick needles, and melts at 72°. Attempts to prepare the oxime were unsuccessful.

Benzenylphenylenediamine (anhydrobenzoyldiamidobenzene), already described by Hübner (Abstr., 1881, 1131), is obtained in almost theoretical yield when an alcoholic solution of orthamidobenzophenone (1 mol.) and hydroxylamine hydrochloride (3 mols.) is heated at 130—140° in a sealed tube for 3—4 hours; its melting point (291°) is higher than that observed by Hübner. The same base is formed in small quantity when orthamidobenzophenone oxime hydrochloride is heated for several hours with alcohol at 150°, or in the presence of a few drops of hydrochloric acid at 130—140°. A. R. L.

A New Series of Hydroxynitro-derivatives of Triphenylmethane and its Homologues. By G. BERTONI (*Gazzetta*, **21**, 167—174).—The author applies Baeyer's method for the preparation of triphenylmethane derivatives by the action of aromatic aldehydes on phenols to metanitrobenzaldehyde, and in this way has obtained derivatives of orcinol and phloroglucinol.

Metanitrophenyldiorcinolmethane, $CH[C_6H_2Me(OH)_2]_2{\cdot}C_6H_4{\cdot}NO_2$, is obtained when the theoretical proportions of orcinol and metanitrobenzaldehyde are gently warmed with sulphuric acid ($H_2SO_4 + 2H_2O$). The crude product is purified by continued washing with boiling water, and subsequent precipitation from its alcoholic and ethereal solutions by water and light petroleum respectively. The pure substance is an amorphous powder of the colour of manganese sulphide, and is soluble in alcohol, ether, acetic acid, and alkalis. It darkens slowly on exposure to air and light, and on heating softens at 241°, but does not melt. The position in the orcinol molecules occupied by the central methane carbon atom cannot be fixed with certainty.

Metanitrophenyldiphloroglucinolmethane, $CH[C_6H_2(OH)_3]_2{\cdot}C_6H_4{\cdot}NO_2$

[OH : OH : CH : OH = 1 : 3 : 4 : 5], is obtained with great readiness by the action of metanitrobenzaldehyde on anhydrous phloroglucinol at about 200°, without any condensing agent; the crude substance is purified in the same way as the preceding compound. It is an amorphous powder, soluble in alcohol, ether, and acetic acid, blackens on heating to 245°, but does not melt, and its ethereal solution darkens rapidly on exposure to air. W. J. P.

Nitro-derivatives of α-Ethoxynaphthalene. By P. HEERMANN (*J. pr. Chem.* [2], **44**, 238—245).—*αα-Ethoxynitronaphthalene* is obtained, together with an isomeride (see below), when α-ethoxynaphthalene is dissolved in 2½—3 times its weight of glacial acetic acid, and treated at a temperature not exceeding 20° with 1½ times the theoretical quantity of nitric acid (sp. gr. 1·43). After repeated crystallisation from alcohol, it forms yellow needles; it melts at 116—117°, is volatile with steam, and is soluble in most organic solvents. The yield is 90 per cent. of the theoretical. When boiled with alcoholic potash, it is converted into the corresponding nitronaphthol (m. p. 164°), and into the nitronaphthylamine (m. p. 191°) when heated with alcoholic ammonia in a sealed tube at 180°.

αβ-Ethoxynitronaphthalene is precipitated on adding water to the glacial acetic acid and alcoholic mother liquors from the αα-derivative. When crystallised from light petroleum, it forms bright-yellow needles, melts at 84°, is volatile with steam, and much more soluble in alcohol than the isomeric compound; the yield is 2—4 per cent. of the total nitration product. On boiling with alcoholic potash, it readily yields the corresponding nitronaphthol melting at 128°, but is not altered when heated for eight hours in a sealed tube at 180—190° with alcoholic ammonia.

ααβ-Ethoxydinitronaphthalene [NO_2 : NO_2 : EtO = 1 : 2 : 4] is formed, together with an isomeride (see below), when αα-nitroethoxynaphthalene is gradually added to six times its weight of nitric acid (sp. gr. 1·43), cooled to −10°; after the mixture has remained at 0° for 2—3 hours, the precipitated crystals are collected, treated with ammonia, boiled with light petroleum, and filtered from the undissolved portion. The compound separates from the filtrate in bright-yellow needles, which melt at 92—93°, or at 88° when finely powdered (compare Martius, *Zeit. Chem.*, 1868, 82); it is soluble in most organic solvents, and sparingly volatile with steam. It is readily converted into the corresponding dinitronaphthol (Martius' yellow) on boiling it with alcoholic potash, and into the dinitronaphthylamine melting at 236° on heating it in a sealed tube with alcoholic ammonia.

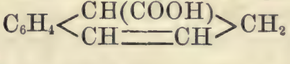
ααα-Ethoxydinitronaphthalene [NO_2:NO_2:EtO = 2:1′:1, or 2 : 4′ : 1] represents the portion of the nitration product insoluble in light petroleum; when crystallised from alcohol with the use of animal charcoal, it forms small, lustrous plates, melts at 188°, and is sparingly soluble in cold alcohol; it forms the smaller portion of the nitration product. α-Nitrophthalic acid is produced when the ethoxy-derivative is heated with nitric acid (sp. gr. 1·14) in a sealed tube at 200°, or when the corresponding dinitronaphthol, obtained by boiling the ethoxy-derivative with alcoholic potash, is oxidised with an alkaline solution of potassium permanganate. Ethoxytrinitronaphthalene, crystallising from alcohol in small, yellow plates melting at 170—171°, and tetranitronaphthol melting at 215° are obtained from the alcoholic filtrate from the last-described dinitro-derivative.

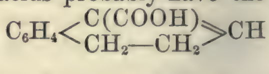
When the above-described $\alpha\beta$-ethoxynitronaphthalene is nitrated, a very small quantity of the dinitro-derivative of melting point 92—93° is formed, but the chief product is a compound melting at 132°. A. R. L.

Hydrogenation of the Naphthoic Acids. By W. v. SOWINSKI (*Ber.*, **24**, 2354—2363).—Preliminary experiments showed that when the naphthoic acids are heated at 200° with hydriodic acid and phosphorus, the products no longer possess acid properties.

Dihydro-α-naphthoic acid is formed when 3 per cent. sodium amalgam (300 grams) is added to a solution of α-naphthoic acid (10 grams) in the requisite quantity of aqueous sodium carbonate, diluted with water (300 grams), and cooled to 0°; the mixture is shaken, and the temperature kept below 5° during the reaction. The solution is nearly neutralised with dilute sulphuric acid, filtered, and an excess of dilute acid added to the cooled filtrate, when the acid separates after a time as a crystalline precipitate. It melts at 76°, and is almost insoluble in cold water, readily in hot; the *silver salt* is a white, voluminous precipitate, slightly soluble in hot water; the *copper salt* is a bright, bluish-green precipitate, very sparingly soluble in water; whilst the *calcium* and *barium salts* are easily soluble. The free acid separates on concentrating the aqueous solution of the *ammonium salt*, and when the latter is heated with a solution of mercuric chloride, the odour of naphthalene is developed. When the acid is distilled over heated soda-lime, naphthalene is produced. It yields a *dibromide* when dissolved in carbon bisulphide and treated with bromine; this is converted into a *monobromhydronaphthoic acid* by cold aqueous sodium carbonate; the last-mentioned acid decomposes, and yields naphthalene when boiled with aqueous sodium carbonate.

When the above described dihydro-α-naphthoic acid is boiled with a dilute solution of sodium hydroxide, or when α-naphthoic acid is treated with sodium amalgam at the ordinary temperature without cooling, a more stable isomeric *dihydro-α-naphthoic* acid is obtained; this melts at 112°, both the acid and the salts closely resembling their isomerides; it yields a crystalline *dibromide*, which melts at 136° with decomposition. Alkalis decompose it in the cold, but more quickly on heating. The two dihydro-α-naphthoic acids probably have the constitution $C_6H_4<\begin{array}{c}CH(COOH)\\CH{=\!=}CH\end{array}>CH_2$ and $C_6H_4<\begin{array}{c}C(COOH)\\CH_2-CH_2\end{array}>CH$ respectively.





Ac.-tetrahydro-α-naphthoic acid is produced when a solution of α-naphthoic acid (7 grams) in amyl alcohol (80 grams) is allowed to drop in a thin stream on to metallic sodium (6 grams), and the mixture boiled. The sodium salt is then dissolved out by shaking with water, the small quantity of amyl alcohol dissolved in the aqueous solution being removed by extracting it with ether; the excess of ether is driven off, and the liquid nearly neutralised, filtered, and an excess of acid added to the filtrate; the oil which separates is then extracted by agitation with ether, and the ethereal solution evaporated, when a hard mass having the odour of valeric acid is left. This is repeatedly dissolved in alkali, and reprecipitated with acid, whereby it is ultimately obtained in the form of small, white needles; it melts at 80°, and is very slightly soluble in cold water, much more so in hot, and very readily in other solvents. The *silver* and *barium salts* are easily soluble in water; the free acid is formed on evaporating a solution of the *ammonium salt*, and naphthalene is obtained on distilling it over soda-lime. The acid is not altered by boiling with water, or with aqueous sodium hydroxide; it forms substitution derivatives with bromine. The same tetrahydronaphthoic acid is obtained when dihydro-α-naphthoic acid (m. p. 112°) is heated with sodium amalgam.

Dihydro-β-naphthoic acid is formed in a similar manner to the α-derivative (m. p. 76°) from sodium amalgam and β-naphthoic acid. It melts at 103°, and is sparingly soluble in cold water, easily in hot water, and in other solvents. The *silver salt* is fairly soluble, and the *copper salt* sparingly so in hot water; whilst the *calcium* and *barium salts* are readily soluble in water. When the solution of the *ammonium salt* is boiled with mercuric chloride, the odour of naphthalene is perceptible. The acid forms a *dibromide*, which appears to be as unstable as the α-derivative of m. p. 76°. A more stable *isomeride* is obtained when the last-described modification is boiled for 5—6 hours with sodium hydroxide solution in a reflux apparatus, or by the action of sodium amalgam at the ordinary temperature on β-naphthoic acid; this melts at 158°, and crystallises from alcohol in small, iridescent plates; when treated with bromine, hydrogen bromide is evolved.

Tetrahydro-β-naphthoic acid is best prepared by boiling dihydronaphthoic acid (m. p. 158°) with sodium amalgam; it is also formed when β-naphthoic acid is dissolved in a large quantity of amyl alcohol, and boiled with sodium. It melts at 94°, forms substitution derivatives with bromine, and is not decomposed by boiling with water or alkalis. All the above hydrogenised acids are oxidised by permanganate in the cold, and the more stable dihydro-acids are less soluble than their isomerides, the tetrahydro-acids being still less soluble; the same applies to the salts. A. R. L.

α- and β-Naphthylazoacetoacetic Acids and their Derivatives. By G. Oddo (*Gazzetta*, **21**, 264—271).—*Ethyl α-naphthylazoacetoacetate*, $C_{10}H_7 \cdot N_2 \cdot CHAc \cdot COOEt$, is prepared by mixing aqueous solutions of α-diazonaphthalene chloride and ethyl sodacetoacetate in molecular proportion; the yield is almost theoretical. When pure, it crystallises from dilute alcohol in bright-yellow, microscopic tables, melts at 93—94° without decomposition, dissolves very freely in alcohol, ether, and benzene, but is insoluble in water. The action of potash on this substance varies with the concentration and with the temperature, either α-naphthylazoacetone or the compound $C_{10}H_7 \cdot N_2 \cdot CH_2 \cdot COOH$ being formed.

α-Naphthylazoacetone, $C_{10}H_7 \cdot N_2 \cdot CH_2Ac$, is prepared by dissolving the preceding compound in a 10 per cent. solution of potash at 100°; on cooling, a dark red precipitate separates, which, after repeated treatment with dilute alcohol and animal charcoal, crystallises in microscopic, elongated, golden-yellow prisms, which melt without decomposition at 158—160°. It dissolves very freely in alcohol, but less so in ether, benzene, &c. It is not altered by boiling with potash.

α-Naphthylazoacetic Acid.—This acid is precipitated in bulky, yellow flakes on adding hydrochloric acid to the mother liquors obtained in the preparation of the preceding compound. The crude product melts at 135—140°, and probably has the composition $C_{10}H_7 \cdot N_2 \cdot CH_2 \cdot COOH$.

Naphthylazoacetoacetic Acid.—The α-naphthyl acid, like acetoacetic acid, decomposes when attempts are made to isolate it; the β-naphthyl acid is, however, more stable. Its *potassium derivative*, $C_{10}H_{11}N_2O_3K + 3H_2O$, is obtained by the action of potash on the corresponding ethyl derivative, which is prepared in a similar manner to the α-naphthyl salt. It crystallises from alcohol in irregular, yellowish plates, and melts with decomposition at 206—208°. The free acid, $C_{10}H_7 \cdot N_2 \cdot CHAc \cdot COOH$, is obtained by hydrolysing the potassium salt; it separates from alcohol in light flakes, consisting of yellow, microscopic, rectangular tables. It melts with decomposition at 198—200°, and dissolves in alcohol, ether, and benzene.

It is to be noted that the analogous azobenzene- and azotoluene-acetoacetic acids prepared by Meyer and Züblin (Abstr., 1878, ii, 880) do not undergo the acid and ketonic decompositions of ethyl acetoacetate. S. B. A. A.

Hydroxy-derivatives of Alizarin-blue. By R. E. SCHMIDT and L. GATTERMANN (*J. pr. Chem.* [2], **44**, 103—109).—*Dihydroxyalizarin-blue*, $C_{17}H_7NO_4(OH)_2$, prepared from amidoquinalizarin (this vol., p. 935), is almost insoluble in the ordinary solvents, and, like the other derivatives of alizarin-blue described in the paper, is best crystallised from nitrobenzene. It forms blue needles, which have a coppery lustre and closely resemble indigo in appearance, and its vapour is violet-blue in colour, like that of iodine. In concentrated sulphuric acid it dissolves with a greenish-blue colour, and the solution shows two marked absorption bands in the red and orange.

A *trihydroxyalizarin-blue*, $C_{17}H_6NO_4(OH)_3$, is obtained when alizarin-blue is warmed with 20 times its weight of 80 per cent. anhydrosulphuric acid at 30—40° for several days. It crystallises from nitrobenzene, and on heating, sublimes in dark-blue needles. In sulphuric acid it dissolves with a greenish-blue colour, similar to that given by dihydroxyalizarin-blue, and the solution gives similar, but somewhat narrower, absorption bands.

The formation of a trihydroxyalizarin-blue by the action of fuming sulphuric acid on alizarin-blue led the authors to examine the colouring matters "alizarin-blue-green," "alizarin-green," and "alizarin-indigo-blue," obtained by the Badische Anilin- und Soda-Fabrik (German Patents, 46654, 47252) by the action of anhydrosulphuric acid on alizarin-blue, with the object of determining not only their nature, but also their relationship to the substance produced from alizarin by the action of the same reagent.

"Alizarin-blue-green," prepared by treating alizarin-blue with 10 times its weight of 70 per cent. anhydrosulphuric acid and warming the product with twice the quantity of sulphuric acid of 66° Baumé for some time at 50—60°, can be readily purified by conversion into its compound with sodium hydrogen sulphite, dissolving this in water, precipitating with salt, repeating the process several times, and finally decomposing with hydrochloric acid. It crystallises well, and is a *hydroxyalizarin-blue-sulphonic acid*, $OH{\cdot}C_{17}H_7NO_4{\cdot}SO_3H$, which, on hydrolysis with concentrated hydrochloric acid at 160—170°, is converted into hydroxyalizarin-blue.

Hydroxyalizarin-blue, $C_{17}H_8NO_4{\cdot}OH$, may also be obtained on the large scale by heating "alizarin-blue-green" with 10 times its weight of sulphuric acid of 60° Baumé (78 per cent. H_2SO_4) at 140—145° for some hours. The product of the reaction is a crystalline *sulphate* of the composition $C_{17}H_8NO_4{\cdot}OH + H_2SO_4$, which, when heated with aqueous sodium acetate for a short time, yields the hydroxy-base.

"Alizarin-green," formed by heating "alizarin-blue-green" with 10 times its weight of pure sulphuric acid (100 per cent. H_2SO_4) for six hours at 120—130°, is readily purified by conversion into its compound with ammonium hydrogen sulphite, which, after dissolution in water, can be precipitated by potassium chloride, and when pure decomposed by hydrochloric acid. It crystallises in slender, greyish-violet, silky needles, and is a *hydroxyalizarin-blue-sulphonic acid*, $OH{\cdot}C_{17}H_7NO_4{\cdot}SO_3H$, isomeric with "alizarin-blue-green," being formed from this by hydrolysis and subsequent sulphonation in another position in the molecule. This is shown by the fact that both the greens, together with hydroxyalizarin-blue, can be isolated from the melt if the reaction is stopped when a test sample dissolved in strong sulphuric acid gives a solution showing the maximum shade of blue. Moreover, on hydrolysis with concentrated hydrochloric acid, "alizarin-green," like "alizarin-blue-green," yields hydroxyalizarin-blue.

"Alizarin-indigo-blue" contains as chief constituent a trihydroxyalizarin-blue isomeric with that just described. When "alizarin-blue-green" is heated with 20 times its weight of sulphuric acid of 66° Baumé at 200—210°, the solution, after a time, gives almost the same absorption bands as the solution of the quinoline derivative of "alizarin-claret" already described; but, on continuing the heating, these become fainter, and at the end of five hours can hardly be observed. The product thus formed is a *trihydroxyalizarin-blue*, $C_{17}H_6NO_4(OH)_3$, which can be crystallised from nitrobenzene. The technical product obtained by heating "alizarin-green" with sulphuric acid at 200—210° contains, in addition to this substance, a sulphonic acid which does not dissolve in nitrobenzene, and on hydrolysis with concentrated hydrochloric acid, yields a *dihydroxyalizarin-blue*, $C_{17}H_7NO_4(OH)_2$, whose absorption spectrum is identical with that of the quinoline derivative of "alizarin-claret." The examination of these colouring matters is being continued. W. P. W.

Essence of Myrtle. By P. BARTOLOTTI (*Gazzetta*, **21**, 276—282).—The essence of myrtle (*Myrtus communis*), when purified by redistillation over calcium chloride, is a colourless, mobile liquid, soluble in alcohol, ether, &c., but only very sparingly in water; the aqueous solution has, however, the strong, characteristic odour of the essence. The sp. gr. of the essence is 0·881 at 27°, and it is dextrorotatory, $[\alpha]_D = +55·4$.

By continued distillation it may be split up into four fractions: *a*, about 19 per cent., passing over at 152—160°; *b*, about 29 per cent., at 160—162°; *c*, about 21 per cent., at 162—165°; and *d*, 26 per cent., at 165—180°. All of these are colourless, neutral liquids, the first only having the odour of myrtle, the others smelling of mint. A small quantity of water always passes over with the first portions of every distillate even if the essence is completely dried before distillation. This takes place even when the distillation is conducted in an atmosphere of carbonic anhydride, and led the author to suspect the presence of an oxidised compound in the essence. The greater part of the fraction *a* consists of a terpene, $C_{10}H_{16}$, which, after purification and repeated redistillation, passes over at 154—155°. It is a colourless, very mobile liquid with a somewhat unpleasant odour, and dissolves in alcohol and ether, but not in water. Its sp. gr. at 27° is 0·857, and its rotatory power $[\alpha]_D = +59·3$. The hydrocarbon distilling at 163°, separated by Gladstone (this Journal, 1864, **17**, 1) from essence of myrtle, appears to contain an admixture of an oxidised compound. On heating it with sodium, a slow reaction takes place, and the residue consists of a terpene, $C_{10}H_{16}$, distilling at 160°. This is a colourless, very mobile liquid with an odour of turpentine. Its sp. gr. at 27° is 0·860, and the specific rotation $[\alpha]_D = +53·6$. The last portions of the distillate from the essence of myrtle yield on fractionation a substance having the composition $C_{10}H_{16}O$. It is a colourless, mobile liquid with an odour of peppermint, and turns yellow when exposed to the light for a time; it dissolves in alcohol and ether, but not in water. Its sp. gr. at 27° is 0·896, and its specific rotatory power $[\alpha]_D = +24·8$. S. B. A. A.

Terebic Acid. By G. CORSELLI (*Gazzetta*, **21**, 271—276).—On heating terebic acid with alcoholic ammonia for six hours at 160—170° and distilling the product on the water-bath, the residue contains an acid compound of the composition $C_6H_{11}O_2N$, which crystallises from water in plates, melts at 204°, and dissolves very freely in alcohol, and moderately in ether. It also dissolves in the alkali hydroxides and carbonates, and in ammonia on heating, and in nitric and concentrated hydrochloric acid on prolonged boiling; from the latter solution, it separates unaltered on cooling. It forms a red solution with sulphuric acid. The *silver* salt, $AgC_6H_{10}O_2N$, forms small, white crystals readily affected by light. On treating the acid with nitrous acid, a nitroso-derivative is formed, which has the composition $C_6H_{10}N_2O_3$. It separates from alcohol in small, colourless crystals which melt at 170°, and give Liebermann's reaction for nitroso-compounds.

When a mixture of terebic acid and aniline in molecular proportion is heated for half an hour at 155°, the product has the composition $C_{12}H_{15}NO$, and crystallises from water in white, prismatic needles, melts at 153—154°, and dissolves in water, alcohol, ether, and benzene. On heating it with a 30 per cent. solution of potash for a few hours, aniline and pyroterebic acid are formed.

The *acetyl derivative*, $C_{12}H_{14}ONAc$, crystallises from water in nodules, melts at 175°, and dissolves in alcohol and ether.

S. B. A. A.

Resin obtained from Thwites' "Doona zeylanica." By E. VALENTA (*Monatsh.*, **12**, 98—106).—This resin was exhibited in the Colonial Exhibition of 1887, held in London. It has a sp. gr. of 1·1362 at 17·5°, and melts on being strongly heated, at the same time turning brown and emitting a pleasant odour. It burns in the air with a brilliant flame, leaving 0·007 per cent. of ash, consisting of the carbonates of calcium and of the alkalis, with a small quantity of oxide of iron.

By successive treatment of the resin with different solvents, three distinct resins may be separated; one of these, the α-resin, has acid properties, whilst the other two, the β- and γ-resins, are neutral substances.

The α-resin is isolated by exhausting the finely-powdered Doona-resin with 4—5 times its weight of 90 per cent. alcohol, at 30—35°. On evaporating the solution thus obtained, it leaves a yellow, friable mass which resembles American colophony in appearance. This melts at 115°, gives, on elementary analysis, numbers corresponding with the formula $C_{24}H_{39}O_2$, is readily soluble in methyl, ethyl, and amyl alcohols and in hot fatty oils, and is readily nitrated by a mixture of nitric and sulphuric acids. The iodine number, determined by Hübl's method, is 60, and 1 gram of the resin requires 0·023 gram of potassium hydroxide to completely neutralise it. On distillation under a reduced pressure of 150 mm., a yellow, oily liquid, containing small quantities of acetic and formic acids, distils over at 110—140°; whilst at a temperature of 180—200°, a solid, light-yellow, neutral resin is the product. The Doona-resin contains about 65 per cent. of the α-resin.

The β-resin is obtained when the residue left in the preparation of the α-resin is exhausted with ether. It forms a colourless, tasteless, and odourless mass, which softens at 120° and melts at 150—160°. It is soluble in ether, benzene, toluene, and xylene, and on elementary analysis gives numbers which correspond with the formula $C_{21}H_{33}O$.

The γ-resin is obtained by treating that portion of the Doona-resin which is insoluble in alcohol and ether with light petroleum; on evaporating, an almost colourless, transparent, brittle mass is obtained, which is insoluble in methyl, ethyl, and amyl alcohols, in ether, acetic acid, and amyl acetate, but dissolves readily in toluene and xylene; these solutions, on evaporation, give a shellac which is colourless and almost unaffected by acids and alkalis. The γ-resin is only slowly dissolved by sulphuric acid, and forms nitro-products with fuming nitric acid. On elementary analysis, it gives numbers corresponding with the formula $C_{31}H_{49}O$. The amount of β- and γ-resins contained in Doona-resin is about 15 and 20 per cent. respectively. It is to be noted that a difference of $C_{10}H_{16}$, the formula for a terpene, exists in the above-given formulæ for the β- and γ-resins.

G. T. M.

Gentisin. By S. v. KOSTANECKI (*Monatsh.*, **12**, 205—210; compare this vol., p. 1244).—*Gentiseïn*, obtained by boiling gentisin with hydriodic acid, melts at 315°. It is soluble in alkalis with a yellow colour, gives a blood-red coloration with sodium amalgam, and a deep-red precipitate with acids. In contradistinction to gentisin, gentiseïn dyes wool a pale-yellow in presence of an aluminium mordant; the hydroxyl group, which in gentisin is methylated, thus appears to have tinctorial properties.

Triacetylgentiseïn, $C_{13}H_5O_2(OAc)_3$, melts at 226°, and is more sparingly soluble than diacetylgentisin.

J. B. T.

Gentisin. By S. v. KOSTANECKI and E. SCHMIDT (*Monatsh.*, **12**, 318—322).—*Dimethoxygentiseïn*, $C_{13}H_6O_3(OMe)_2$, can be obtained by heating gentiseïn or gentisin with potash and methyl iodide in methyl alcoholic solution at 100°; it crystallises from glacial acetic acid in broad, yellow needles, melts at 167°, and is sparingly soluble in alcohol; its alkali derivatives are intensely yellow compounds.

The *acetyl* derivative, $C_{13}H_5O_2(OMe)_2{\cdot}OAc$, crystallises from alcohol in colourless needles, and melts at 189°.

F. S. K.

Quercetin and its Derivatives. By J. HERZIG (*Monatsh.*, **12**, 172—176 and 177—190).—Quercetin is probably represented by the formula $C_{15}H_{10}O_7$, for this agrees better with the analytical results than Löwe's formula $C_{15}H_{12}O_7$. That the molecular weight is not represented by a multiple of 292 is shown by determinations of the boiling points of solutions of quercetin and acetylquercetin ethyl ether in ethyl alcohol. The old formula for quercetin is $C_{24}H_{16}O_{11}$, for fisetin $C_{23}H_{16}O_9$; there is thus a difference of CO_2; chemically, however, quercetin behaves like a hydroxy-fisetin; this difficulty disappears if the formula for quercetin given above is adopted. The following results prove that in all probability fisetin has the formula $C_{15}H_{10}O_6$, and that quercetin is a monhydroxy-derivative. The author is able to confirm Schmidt's observations on fisetin, but fisetin methyl ether can be obtained in long, colourless, glistening needles melting at 151—153°, by repeated recrystallisation from alcohol. The ethyl ether yields fisetin on treatment with hydriodic acid. Protocatechuic acid and resorcinol are formed when fisetin is dissolved in potash, and the solution allowed to remain exposed to the air for 24 hours, whilst quercetin, under similar conditions, yields protocatechuic acid and phloroglucinol.

On heating ethoxyfisetin, $C_{15}H_6O_2(OEt)_4$, on the water-bath with 10 parts of alcoholic potash for 7—8 hours, and saturating the solution with carbonic anhydride, a compound is deposited which is termed *fisetol ethyl ether*; it crystallises from dilute alcohol in colourless needles, melts at 42—44°, and gives a pale-red coloration with ferric chloride, which disappears on the addition of alkali carbonates. The mother liquors from the phenol contain diethoxyprotocatechuic acid.

Fisetol diethyl ether has the formula $C_8H_6O_2(OEt)_2$, and appears to be derived from *fisetol*, $C_8H_5O(OH)_3$, which has not yet been isolated; it is probably a resorcinol derivative, with one hydroxyl group in a side chain, and contains an aldehydic or ketonic group. *Fisetol triethyl ether*, $C_8H_5O(OEt)_3$, is prepared by the action of potash and ethyl iodide on the diethoxy-derivative; it crystallises from dilute alcohol in long needles melting at 66—68°, decomposes on further heating, and is not hydrolysed by alcoholic potash.

Fisetol dimethyl ether, $C_8H_6O_2(OMe)_2$, is prepared from *fisetin tetramethyl ether* in a similar manner to the ethyl derivative; it crystallises in small, colourless needles which melt at 66—68°. The *trimethoxy-derivative* is deposited from dilute alcohol in small, colourless needles melting at 62—63°, and is unacted on by potash.

Fisetol dimethyl ethyl ether, $C_8H_5O(OMe)_2{\cdot}OEt$, crystallises in lustrous needles melting at 60—62°.

J. B. T.

The Bark of Gonolobus condurango. By G. CARRARA (*Gazzetta*, **21**, 204—212).—The bark is extracted with strong alcohol, and the filtered solution allowed to cool; a greenish powder (A) falls, leaving a yellowish-brown solution (B). On treating A with ether, it is divided into a soluble part (*a*), and a yellowish, insoluble powder (*b*); the latter is purified by dissolving it in boiling alcohol, allowing the solution to cool, and washing the deposit repeatedly with alcohol and ether. It proves to be a glucoside of the composition $C_{40}H_{74}O_6$, which melts at 112°, and is insoluble in ether and light petroleum, sparingly soluble in cold alcohol, and very slightly in water; the aqueous solution is not precipitated by potassium mercuric iodide, or by a solution of iodine and potassium iodide. When boiled for some hours with dilute sulphuric acid, the liquid reduces Fehling's solution.

The glucoside, when heated with benzoic chloride at 100°, forms a benzoyl derivative, $C_{40}H_{73}O_6Bz$; this can be purified by precipitation from its solution in chloroform by alcohol. It is a brownish-red powder, insoluble in alcohol, water, and light petroleum, very soluble in chloroform, but only sparingly in ether; it blackens at 250°, and melts with decomposition above 270°. On evaporating the mixture of alcohol and chloroform from which this compound is deposited, a white powder is left, which melts at 72°, and yields benzoic acid when boiled with potash solution; a sufficient quantity for complete examination could not be obtained.

The substance *a* is boiled with alcoholic potash, the alcohol evaporated, the residue taken up with water, and extracted with ether; on evaporation, a yellow powder is obtained, showing the colour reactions of chloresterol, but melting at 52° and having the composition $C_{30}H_{50}O_2$; this compound the author names *conduransterin*.

The aqueous solution remaining after extraction of the conduransterin by ether contains cinnamic acid.

The original extract B has not yet been fully examined.

W. J. P.

Synthesis of Ethylpyrroline. By C. U. ZANETTI (*Gazzetta*, **21**, 248—250).—The author has previously shown (Abstr., 1890, 202) that the product of the action of ethyl iodide on potassium pyrroline contained

1-ethylpyrroline, together with a quantity of another ethylpyrroline, which it was not found possible to identify with certainty. By the action of acetic anhydride, two products are obtained, in which the acetyl is united to carbon and nitrogen respectively; the former boils between 245° and 255°, and the latter between 200° and 240°. The first of these was converted into the *cinnamyl* derivative,

$$CHPh{:}CH{\cdot}CO{\cdot}C_4NH_3Et,$$

by heating with benzaldehyde and potash. The product, when pure, crystallises in yellow, lustrous needles melting at 150°, and soluble in boiling alcohol and ether, but not in water. On treating its alcoholic solution with a similar solution of silver nitrate, and adding a few drops of alcoholic ammonia, the silver derivative separates as a bulky, yellow precipitate. This ethylpyrroline is consequently identical with that prepared by Dennstedt and Zimmermann (Abstr., 1886, 1043), by the action of paraldehyde on pyrroline in presence of zinc chloride.
S. B. A. A.

Pyridinebetaïnes. By M. Krüger (*J. pr. Chem.* [2], **44**, 130—136; compare this vol., p. 941).—Hofmann (Abstr., 1881, 921) has also noticed the production of a blue colour when alkylpyridylammonium halides are reduced with sodium amalgam in aqueous solution (compare this vol., p. 941). The author has further investigated the conditions under which this coloration is produced, and summarises the results of his experiments as follows:—All pyridine compounds formed by the addition of pyridine to halogen-substitution derivatives of the alkyl series give a blue colour when reduced with sodium amalgam, zinc-dust, or iron-dust in aqueous or alcoholic solution; the products of the reduction are double bases, formed by the combination of two pyridine rings through the opening out of a double bond in each ring (compare Abstr., 1881, 921). This colour reaction furnishes a convenient method for deciding whether a substance under investigation is a *pyridonium* compound or not.

The alkyliodides of the homologues of pyridine give double bases of the same nature when they are reduced with sodium amalgam, but no coloration has been noticed by the author, and Hofmann does not mention whether a change of colour occurs or not.

Pyridinechlorhydrin, $C_5NH_5Cl{\cdot}C_3H_5(OH)_2$, is formed when monochlorhydrin is heated for 6—8 hours with pyridine at 125—130°; it crystallises from alcohol in small, feebly lustrous, six-sided, apparently rhombohedral crystals, melts at 105—107°, and dissolves in water and alcohol, but not in ether. Its aqueous solution gives an intense-blue colour with sodium amalgam, if warm, and a purple-violet in the cold. The free base, obtained by treating the chlorhydrin with moist silver oxide, is strongly alkaline, and precipitates the oxides of the heavy metals; it can, however, only be obtained in dilute solution, for it decomposes when concentrated. The *platinochloride*, $C_8H_{10}O_2N,H_2PtCl_6$, forms lustrous, orange-red scales, and melts at 180° (uncorr.) with decomposition; the *aurochloride* forms lemon-yellow, feebly-lustrous scales, and melts at 122°.

Both pyridinechlorhydrin and pyridinecholine are converted into pyridinebetaïne when oxidised with chromic acid in sulphuric acid solution. A. G. B.

Oxidation of Quinoline Derivatives. By G. v. GEORGIEVICS (*Monatsh.*, **12**, 304—317).—The behaviour of a number of quinoline derivatives on oxidation has been investigated, with the following results:—

When para- and ana-quinolinebenzocarboxylic acid are oxidised with potassium permanganate under various conditions, some of the acid is completely destroyed, but quinolinic acid is not produced in either case; paratoluquinoline yields paraquinolinebenzocarboxylic acid as the principal product, but no quinolinic acid is formed.

When orthoquinolinebenzocarboxylic acid is oxidised with potassium permanganate in concentrated sulphuric acid solution, quinolinic acid is obtained; when, however, quinoline is treated with the oxidising agent in dilute sulphuric acid solution, it yields metaquinolinebenzocarboxylic acid (m. p. 246°), the formation of which is probably due to the production of a diquinolyl as an intermediate product.

On treating paraquinolinebenzocarboxylic acid with potassium permanganate in alkaline solution, it gives quinolinic acid and a carboxy-derivative of nitrobenzene; the latter compound is also formed in some of the other reactions referred to above, but it is obtained in such small quantities and is so difficult to purify that its composition could not be determined.

When paraquinolinesulphonic acid is oxidised with potassium permanganate in alkaline solution, it yields oxalic acid, very small quantities of quinolinic acid, and the nitrobenzene derivative just mentioned.

These and other experiments proved that the formation of quinolinic acid by the oxidation of quinoline with potassium permanganate, and also of those derivatives which are obtained from it by substituting hydrogen in the benzene nucleus, is, in some cases, dependent on the conditions of the experiment, but that in others quinolinic acid is not formed under any circumstances; the position and the nature of the substituting group also have a considerable influence on the course of the reaction. F. S. K.

Ichthulin. By G. WALTER (*Zeit. physiol. Chem.*, **15**, 477—494).—Ichthulin, the chief proteïd constituent of the yolk of fishes' eggs, was prepared in large quantities by Valenciennes and Frémy (*Compt. rend.*, **38**, 471) from salmon roes, and subjected to elementary analysis. The results of analysis in the present research gave the following percentage results:—

	C.	H.	N.	O.	S.	P.	Fe.
I	53·52	7·71	15·64	22·19	0·41	0·43	0·10
II	53·33	7·56	15·63	23·48			

The general properties of the substance show that it belongs to the class of vitellins. On peptic digestion, it yields, as vitellin does, a nucleïn, which differs from the nucleïn of nuclei in yielding no nitrogenous bases like guanine, adenine, &c., on further decomposition. Simultaneously with the appearance of this para-nucleïn, a reducing carbohydrate is formed. W. D. H.

The Proteïds or Albuminoïds of the Oat Kernel. By T. B. Osborne (*Amer. Chem. J.*, **13**, 385—413).—In this, the concluding portion of his memoir (this vol., p. 1285), the author fully describes the extraction of the various proteïds from oats, and reviews the whole subject in a summary, of which the following is an abstract:—

1. The proteïd removed from freshly-ground oats by direct extraction with weak alcohol—called glutin by Norton—when dehydrated by absolute alcohol and dried over sulphuric acid, is a light-yellowish powder, insoluble in water and absolute alcohol, but soluble in mixtures of alcohol and water and in dilute acids and alkalis, from which it is thrown down on neutralisation. It separates from its solution in 60 per cent. alcohol, by evaporation, as a yellowish, slimy mass. It is remarkable for its content of sulphur (see below), in which it is only exceeded by keratin among the proteïds.

2. When the above substance is heated with dilute alcohol for some time, it coagulates and becomes insoluble in that liquid, but without apparent change of composition. The oat-gliadin of Kreusler and Ritthausen was a product of the further alteration of this substance by the treatment it received to purify it.

3. If oats are first treated with water or 10 per cent. solution of common salt, before extraction with dilute alcohol, the proteïd soluble in alcohol undergoes alteration; the resulting substance is much more soluble in dilute alcohol than that mentioned in 1, and is not transformed into an insoluble modification. When wet with absolute alcohol, the moisture attracted from the air makes it gummy, unlike 1. In composition it is nearly the same as the gliadin, or plant-gelatin, obtained by Dumas and Cahours and by v. Bibra.

4. Weyl states that the chief proteïd extracted by cold 10 per cent. solution of salt behaves towards reagents like the myosin-globulin from animal muscle; this is so, but it coagulates at 80—100°, which is higher than the temperature at which animal myosin coagulates (55—60°). This proteïd appears to be the result of a transformation similar to that by which myosin is formed from myosinogen, and is very similar to myosin in composition; 1·3 per cent. was the most obtained.

5. The proteïd extracted, after complete exhaustion of the oats with alcohol of 0·9 sp. gr., by 10 per cent. salt solution and that dissolved by dilute potash have so nearly the same composition as the globulin extracted by salt solution directly, that they may be regarded as originally identical, 4 (see below) representing the soluble, and 5 and 5*a* the insoluble, or "albuminate," form.

6. When ground oats are directly extracted by dilute potash, without previous treatment with water or dilute alcohol, nearly the whole of the proteïds is dissolved. The substance so extracted, after completely removing the substance soluble in dilute alcohol, is perhaps the

same as the avenine of Johnston and Norton, who extracted oats with dilute ammonia.

7. One hour's treatment of oats with water rendered one-half, and 24 hours' treatment two-thirds, of the proteïds insoluble in 0·2 per cent. potash solution. The portion soluble in potash after action of water (and removal of the proteïd soluble in alcohol) has the same composition as the globulin soluble in salt solution (see below). It is probably the same substance as Kreusler's oat-legumin, and Norton's "proteïn substance," extracted by dilute ammonia.

8. When ground oats are extracted with 10 per cent. solution of salt at 65°, a proteïd separates, on cooling, in the form of spheroids; it differs in composition and properties from all proteïds hitherto described; it dissolves in pure water, is precipitated therefrom by a little salt, redissolved by a further addition, and completely precipitated by saturation with salt. In presence of a little salt and acetic acid, it dissolves in alcohol of 0·9 sp. gr. It has been obtained crystallised in regular octahedra, from solutions in distilled water, as well as from those in salt solution.

9. The aqueous extract of ground oats was found, in agreement with Norton and Kreusler, to contain very little proteïd matter; what is dissolved appears to be, first, an acid-albumin; second, a globulin or globulins similar in reactions to that extracted by 10 per cent. salt solution; and third, a proteose. No true albumin was found in the water extract.

10. In the salt extract, a very small amount of a substance having the reactions of albumin was found, but not analysed.

The following table gives the composition of the proteïds from the oat kernel referred to in this paper; the number at the head of each column denotes the proteïd described in the correspondingly numbered paragraph above:—

	1.	2.	3.	4.	5.	5*a*.	6.	7.	8.
Carbon	53·06	53·10	53·70	52·34	52·48	52·45	53·49	52·49	52·22
Hydrogen	6·94	6·91	7·00	7·21	6·94	6·92	7·01	7·10	6·98
Nitrogen......	16·38	16·49	15·71	16·88	16·85	16·63	16·39	17·11	17·85
Sulphur	2·26	23·50	1·76	0·88	0·57	0·81	0·99	0·80	0·77
Oxygen	21·38		21·83	22·69	23·16	23·19	22·12	22·50	22·18
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

A. G. B.

The Viscous Material formed by the Bacterium gliscrogenum. By P. MALERBA (*Zeit. physiol. Chem.*, **15**, 539—545).—Large quantities of the slimy substance, gliscrin, formed by the growth of the *B. gliscrogenum* were obtained by growing it in urine. Alcohol was then added, the precipitated material dissolved in water, reprecipitated by alcohol, and well washed with alcohol and water acidified with acetic acid. After long standing under concentrated alcohol, it becomes insoluble in water. It is nitrogenous, and gives the various proteïd reactions. Albertoni at one time considered that it was a carbohydrate, and it is possible that in the impure state there may be carbohydrate mixed with it, but no direct proofs of this were found in the present research. W. D. H.

Physiological Chemistry.

Formation of Lactic Acid and Glucose in the Organism. By T. Araki (*Zeit. physiol. Chem.*, **15**, 546—561; compare this vol., p. 1125).—In the research of which this is the continuation, the diminution of oxygen in the body was shown to be a cause of the appearance of sugar and lactic acid in the urine. Morphine and other narcotics have often been observed to produce glycosuria. It is now shown that they also cause the appearance of lactic acid in the urine; thus the cause of the glycosuria is probably here also a diminution of oxygen in the organism. The animals used were frogs, rabbits, and dogs. The drugs employed were morphine, amyl nitrite, and cocaïne, and of these amyl nitrite is especially powerful in producing excretion of lactic acid. W. D. H.

Carbohydrates in the Urine. By E. Roos (*Zeit. physiol. Chem.*, **15**, 513—538).—The normal urine of the dog, rabbit, and horse contains a certain quantity of carbohydrates, most in the dog, least in the rabbit.

The results obtained by the furfuraldehyde reaction were confirmed by the benzoic chloride method.

With human urine, the phenylhydrazine reaction always gives a positive result. The same is true for dog's urine. Rabbit's urine gives especially well-formed crystals. In the case of the urine of the dog and horse, preliminary precipitation by lead acetate is necessary. The urine of all these animals is slightly lævorotatory.

W. D. H.

Influence of Wool on the Material Exchange of Sheep. By E. Kern, H. Wattenberg, and T. Pfeiffer (*Bied. Centr.*, 1891, 451—454).—The amount of carbonic anhydride and nitrogen excreted by sheep when clothed with wool, immediately after shearing, and some considerable time after shearing, was determined. It was found that the production of carbonic anhydride increased considerably immediately after shearing; but when the sheep became accustomed to the new state of affairs, then the excretion fell to the normal amount. There was a slight reduction in the nitrogen excreted after shearing, and the amount of perspiration was considerably less.

E. W. P.

Production of Leucocytosis in Mammals. By J. Horbaczewski (*Monatsh.*, **12**, 221—275).—See p. 1340.

Action of Definitely-related Chemical Compounds on Animals. By W. Gibbs and E. J. Reichert (*Amer. Chem. J.*, **13**, 361—370).—In this continuation of the authors' thesis (this vol., p. 1280), the action of the substances named hereunder on the respiration and circulation of frogs and dogs when administered subcutaneously, intravenously, and internally, is described.

Sodium Nitroprusside.—The fatal dose by the stomach is about 0·2 gram per kilo. of body-weight; by the vein, from 0·1—0·2 gram per kilo. The respirations are increased, the temperature falls, paralysis and general collapse supervene, and death ensues from failure of the heart's action.

Nitroso-β-naphthol.—When given to the dog by the stomach the blood is discoloured, becoming very dark, and exhibiting by means of the spectroscope the presence of nitrite of hæmoglobin. The fatal dose, subcutaneously, is about 0·4 gram per kilo., and is, relatively, very large, owing to slowness of absorption; the heart's action becomes sluggish, the motor reflexes are weakened and, finally, abolished, the heart being arrested in diastole. Intravenously, about 0·04 gram per kilo. is fatal. Internal administration causes persistent vomiting, which prevents determination of the fatal dose. Death is due to paralysis of the respiratory centres.

Nitromethane.—The minimum lethal dose is from one-half to 1 c.c. per kilo. of body-weight. Lassitude, drowsiness, and vomiting occur; sleep passes into stupor, and then into coma, respiration fails, and the heart ceases to beat.

Nitrosodiethylene.—The minimum fatal subcutaneous dose is less than 1 c.c. per kilo.; intravenous, from one-third to one-half c.c. per kilo. Its action is somewhat similar to that of nitromethane.

Hydroxylamine.—The blood becomes much discoloured, almost black, owing to formation of methæmoglobin; general paralysis occurs, and death supervenes from a failure of respiration. The lethal internal dose for the dog is about 0·2—0·3 gram per kilo.; intravenously it is 0·06 gram per kilo.

Aldehyde-ammonia.—The lethal dose subcutaneously injected is 0·15—0·2 gram per kilo.; intravenously injected, it is about 0·04 gram per kilo. Blood pressure, pulse, and respiration rapidly fail, and death results primarily from paralysis of the respiratory centres.

Furfuraldehyde Sodium Hydrogen Sulphite.—The lethal dose, intravenously, is 0·3—0·5 gram per kilo.; 3 grams per kilo. injected subcutaneously killed a dog within 24 hours. There is a decrease of pulse, respiration, and temperature; repeated doses cause further reductions, and death ensues from cardiac paralysis.

Oxamic acid and *cyanuric acid* may be considered inert.

Alcohols.—The action of all the alcohols which the authors have examined is identical with that of ethyl alcohol, but different in degree. Dogiel (*Pflüger's Arch.*, **8**, 605) found that methyl alcohol was the least toxic of the first five alcohols, and amyl alcohol the most. Dujardin-Beaumetz and Andigé (*Compt. rend.*, **83**, 80—82) found that methyl alcohol was less poisonous than ethyl alcohol, and that, in passing from ethyl to amyl alcohols, toxicity regularly increased. The minimum lethal doses of the alcohols which were examined by the authors were, when intravenously injected, as follows in c.c. per kilo. of body-weight:—Propyl, 1·6—2·5; isopropyl, 1·3—2; butyl, 0·3—0·6; isobutyl, 0·6—0·7; secondary butyl, 1·0—1·5; tertiary butyl, 1·0—1·2; heptyl, 0·1—0·12; octyl, 1·05—0·1 (*sic*); allyl, 0·2—0·24; benzyl, 0·4—0·6; cuminyl, 0·25—0·3. A. G. B.

Chemistry of Vegetable Physiology and Agriculture.

Secretions of Microbes; Transformation and Elimination of Organic Matter by the Pyocyanic bacillus. By A. Arnaud and A. Charrin (*Compt. rend.*, **112**, 1157—1160).—When the pyocyanic bacillus acts on asparagine (this vol., p. 1132) 72·5 per cent. of the carbon is eliminated in the form of carbonic anhydride; 13·8 per cent. forms part of the protoplasm of the microbes and the remainder exists in the form of soluble compounds. The quantity of oxygen absorbed is in proportion to the quantity of carbonic anhydride evolved. In a vacuum, evolution of carbonic anhydride takes place slowly; in an atmosphere of carbonic anhydride there is no development of the microbe; in hydrogen there is considerable development, with formation of ammonia.

With gelatin and the necessary salts, the evolution of nitrogen is more regular than with asparagine, but the quantity of ammonia does not increase after the 22nd day. The quantity of nitrogen converted into ammonia is 70 per cent., whilst with asparagine it is 91 per cent. On the other hand, the weight of the microbes and of the products of secretion is considerably greater with gelatin than with asparagine. No pigment is formed, but the products of secretion have marked toxic action. The volatile portions and the portions soluble in alcohol are toxic in large doses and protective in small doses; the portion insoluble in alcohol is toxic, and has no vaccinating effect in small doses. C. H. B.

Substitution of Manganese for Iron in Plant Nutrition. By G. Spampani (*Staz. Sper. Agrar.*, **19**, 5—33).—Water culture experiments were made with oats, white lupins, and maize. There were three series of experiments: in the first (A), the plants were grown in a solution of potassium phosphate (5 grams), calcium nitrate (8 grams), magnesium sulphate (1 gram), and potassium chloride (0·5 gram), 14·5 grams of the mixed salts being dissolved in 14·5 litres of water; in the second series (M), the same solution was employed, with the addition of 7 or 8 drops per litre of manganese sulphate solution (about 0·05 per cent.); in the third (F), ferric chloride was used in the place of manganese.

The appearance of the plants at various periods of growth is described. It was found that the ashes of the leaves of plants grown with manganese gave an intense manganese reaction. But in all cases it was found that manganese could not take the place of iron in the formation of chlorophyll. N. H. M.

Physiology of the Tannins and Trihydroxybenzenes. By E. NICKEL (*Chem. Centr.*, 1891, i, 1041; from *Bot. Centrabl.*, 1891, 1—4).—The author has already expressed the opinion that the tannins are derived from the trihydroxybenzenes, some being derivatives of the symmetrical phloroglucinol, others being derived from pyrogallol and hydroxyquinol, and the tannins may be, therefore, divided into those which have a "symmetrical" origin, and those of an unsymmetrical origin. The tannins do not show any difference in their chemical reactions, however.

The author further expresses the opinion that phloroglucinol is derived from inosite, which, according to Maquenne, is readily converted into tri-iodobenzene and aromatic compounds.

J. W. L.

Experiments with Green Maize. By Z. v. SZILASSY and A. ÇSERHÁTI (*Bied. Centr.*, 1891, 463—469).—Of all fodder plants which have a low percentage of proteïds, but a heavy total yield, maize takes the first place; all others are either below it in quality or in total yield. When thickly sown, maize requires much water, and, therefore, a wet soil is necessary; but the thicker the sowing is, the smaller are the individual plants; although, at the same time, the total yield is better than when the plants stand further apart.

The earlier ripening kinds, as Cinquantino and Székler, are of better quality than the later ripening sort. E. W. P.

Formation of Nitrates in Soils. By A. MÜNTZ (*Compt. rend.*, **112**, 1142—1144).—Nitrites are only found in soils in very small quantities and under exceptional circumstances, whilst on the other hand when the nitrifying organisms are introduced into cultivation fluids, large quantities of nitrites are formed.

Dilute solutions of calcium nitrite undergo no change when left in contact with oxygen for many months. Calcium nitrite is, however, decomposed by carbonic acid with liberation of nitrous acid, a relatively large quantity of carbonic acid being necessary in order to secure complete decomposition. Simultaneous action of oxygen or air and carbonic anhydride on solutions of calcium nitrite completely convert it into nitrate, oxidation taking place when nitrifying organisms are entirely absent.

If calcium nitrite is added to a soil which has previously been heated for half an hour at 100° in order to kill the nitrifying organisms without killing those which produce carbonic anhydride, the nitrite after a few days is completely converted into nitrate.

It seems highly probable, therefore, that the nitrifying organism converts the nitrogen into nitrites, and the latter are converted, without any further action of any organism, into nitrates by the simultaneous action of the oxygen and carbonic anhydride which are always present in soils. C. H. B.

Depreciation of Manure by Exposure to Wet and Fermentation. By ROBERTS and WING (*Bied. Centr.*, 1891, 437—438).—

Horse stable manure was exposed to the weather in a box in a manure heap; there was, after the lapse of half a year, a loss in total weight, an increase in water, and a decrease in the percentage of valuable matter. When horse and cow manure were treated under like conditions, but the drainage collected, there was found to be a loss of the nitrogen to the extent of 3·2 per cent., of the phosphoric acid 4·7 per cent., and of the potash 35 per cent. But *thin* layers of manure exposed to the sun and air and rain lost scarcely anything. E. W. P.

Analytical Chemistry.

Strength of Solutions estimated by their Refraction. By H. O. G. ELLINGER (*J. pr. Chem.* [2], 44, 152—157).—See p. 1305.

Electrolytic Separations. By E. F. SMITH and F. MUHR (*Amer. Chem. J.*, **13**, 417—422).—The most favourable result, together with the conditions under which it was attained, is here quoted from the list of experiments given in each case.

Gold from Palladium.—Gold present, 0·1162 gram; potassium cyanide, 1·50 grams; total volume, 150 c.c.; current in c.c. OH gas per minute, 0·8; palladium present, 0·12; gold found, (1) 0·1162, (2) 0·1163, (3) 0·1162, (4) 0·1163 gram.

Gold from Copper.—Gold present, 0·1725 gram; potassium cyanide, 1·50 grams; total volume, 150 c.c.; OH gas per minute, 0·8 c.c.; copper present, 0·125 gram; gold found, 0·1725.

Gold from Cobalt.—Gold present, 0·1792 gram; Potassium cyanide, 3 grams; total volume, 150 c.c.; OH gas per minute, 0·6 c.c.; cobalt present, 0·15—0·2 gram; gold found, 0·1789.

Gold from Nickel.—Gold present, 0·1725 gram; potassium cyanide, 2·5 grams; total volume, 150 c.c.; OH gas per minute, 0·5 c.c.; nickel present, 0·1373 gram; gold found, 0·1724 gram.

Gold from Zinc.—Gold present, 0·1792 gram; potassium cyanide, 3 grams; total volume, 150 c.c.; OH gas per minute, 0·6 c.c.; zinc present, 0·2 gram; gold found, 0·1790 gram.

Gold from Platinum.—Gold present, 0·1467 gram; potassium cyanide, 2·5 grams; total volume, 150 c.c.; OH gas per minute, 1 c.c.; platinum present, 0·2433 gram; gold found, 0·1468 gram.

Silver from Platinum.—Silver present, 0·077 gram; potassium cyanide, 2·5 grams; total volume, 150 c.c.; OH gas per minute, 1 c.c.; platinum present, 0·2433 gram; silver found, 0·0772 gram.

Cadmium from Platinum.—The precipitated cadmium always contained platinum. (Compare Abstr., 1890, 1029.)

Mercury from Platinum.—Mercury present, 0·1902 gram; potassium cyanide, 2·5 grams; total volume, 150 c.c.; OH gas per minute, 0·2 c.c.; platinum present, 0·2433 gram; mercury found, 0·1900 gram.

Details of difficulties met with in some of these separations will be found in the original paper. A. G. B.

Estimation of Nitrogen in Nitrates by Kjeldahl's Method. By L. F. Kebler (*Chem. News*, **63**, 302—303).—Having investigated various points, the following conclusions are arrived at:—1. Kjeldahl's method is not as accurate as the absolute method for estimating nitrogen in nitrates, but is executed much more rapidly, and is applicable for all practical purposes. 2. To avoid loss of nitric acid, the sulphuric acid must be added quickly. 3. The end of the condenser should dip into the liquid in the receiver. 4. The addition of a metallic oxide economises time. 5. The potassium permanganate must be added to complete oxidation. 6. It is unnecessary to add zinc to the contents of the distillation flask, in order to prevent bumping. D. A. L.

Estimation of Total Phosphoric Acid in Manure. By F. Martinotti (*Staz. Sper. Agrar.*, **19**, 614—616).—The ammonium molybdate method when employed in estimating the total phosphoric acid in manures is liable to error when a certain amount of iron is present, owing the formation of a ferric phosphate insoluble in nitric acid. This is precipitated when the hydrochloric acid used for the extraction of the phosphates is driven off by nitric acid. Analyses of basic slag and mineral phosphates are liable to this error. The following method is recommended:—5 grams of the manure suspended in water (15 c.c.) is treated with hydrochloric acid (30 c.c.) and boiled for half an hour. The whole is evaporated to dryness on a water-bath and again treated with acid (20 c.c.) and evaporated to dryness. The residue is moistened with hydrochloric acid (5 c.c.), treated with boiling water (15 c.c.), heated on a water-bath for 10 minutes, filtered, and washed with boiling water. The filtrate is diluted to 100 c.c.; of this 50 c.c. is treated with aqueous ammonium citrate (125 c.c.; 1 c.c. = 0·4 gram of citric acid), neutralised with ammonia, and diluted to 250 c.c.; a portion of this solution (100 c.c.) is then treated with distilled water (50 c.c.), ammonia (50 c.c.), and magnesia mixture (50 c.c.), well stirred, and left for 12 hours, after which it is filtered and the ammonium magnesium phosphate determined as usual. The method gives very concordant results.

N. H. M.

Note.—The formation of tetrahydrated ferric phosphate was already shown by Arth to be a probable source of error in the estimation of phosphates in slags (Abstr., 1890, 292). N. H. M.

Estimation of Silica in presence of Iron. By Leclere (*Compt. rend.*, **112**, 1132—1133).—The decomposition of ferric chloride in the estimation of silicon can be prevented by adding potassium chloride, which forms the double ferric potassium chloride. 1 gram of metal is dissolved in 20 c.c. of nitric acid and 10 c.c. of hydrochloric acid and boiled with two successive quantities of 30 c.c. of hydrochloric acid in order to expel the greater part of the nitric acid. It is then mixed with 3 grams of ammonium chloride and evaporated to dryness to expel the last traces of nitric acid. The residue is dissolved in hydrochloric acid, mixed with 3 grams of potassium chloride and some water, and again evaporated to dryness. The residue is treated with strong hydrochloric acid and afterwards with water.

If ammonium chloride is not present, the silica may contain manganese, and if all the nitric acid has not been expelled, it may contain potassium. Chromium redissolves completely if the residue is treated with strong hydrochloric acid, but solution is rendered certain by reducing a small quantity to chromous chloride by adding zinc or aluminium. C. H. B.

Alkalimetry of the Blood. By H. Winternitz (*Zeit. physiol. Chem.*, **15**, 505—512).—The alkalinity of the blood was determined by titration with decinormal tartaric acid instead of a mixture of sodium sulphate and tartaric acid, as recommended by v. Jaksch (*Zeit. Klin. Med.*, **13**); the blood is received from the vessel of a living animal through a graduated pipette provided with a stopcock. Provided small quantities are employed, this is available for clinical use. The reaction is determined by litmus paper. The mean alkalinity of 100 c.c. of normal rabbit's blood is 0·165 gram. It is well known that the alkalinity of the blood decreases on coagulation; this diminution is stated to take place in two stages, namely, before and during coagulation. If, however, the alkalinity of fresh blood be immediately neutralised, no further change in reaction occurs. Further, the diminution of alkalinity takes place even though coagulation is hindered by addition of salt solution, but the diminution is not so great as when coagulation occurs. A further question, whether the quantity of oxygen present influenced the result, is answered in the negative.

W. D. H.

Estimation of Sodium Chloride in Wine. By J. Gondoin (*J. Pharm.* [5], **24**, 8—10).—Test paper is prepared by painting filter paper in streaks with a 10 per cent. solution of potassium chromate; this paper should only be prepared in small quantity at a time and should be kept in well-stoppered blue or yellow bottles. A standard solution of silver nitrate is employed (7·25 grams per litre) such that 4 c.c. precipitates 0·01 gram of chlorine, corresponding with 1 gram of sodium chloride per litre, the assay being made on 10 c.c. of wine. The silver solution is run into the wine until a drop of the mixed liquid placed on the test paper gives a brick-red precipitate in addition to the reddish-grey due to the wine alone. J. T.

Decomposition of Chromite by the Electric Current. By E. F. Smith (*Amer. Chem. J.*, **13**, 414—417; compare Abstr., 1889, 926).—30—40 grams of stick potash is melted in a nickel crucible and gently heated until the excess of moisture has been expelled. The crucible is held in a heavy copper wire ring attached to the anode of a storage cell, and is heated by a small flame throughout the decomposition. From 0·1 to 0·5 gram of the finely-divided chromite is brushed from a watch glass upon the liquid alkali, the crucible covered with a perforated glass, and a platinum rod, attached to the cathode, lowered into the melted mass. The current, which should not exceed 1 ampère, is then set in action and continued for 30 to 40 minutes; particles projected from the surface of the melt by the bursting gas bubbles will be returned to the crucible by the drops which collect on, and fall from, the glass cover. Before finally interrupting the current, it should be reversed for a short time by means of a commutator; this is because metallic iron is deposited on the cathode and may enclose particles of the ore, which will thus remain unattacked.

After the current has been interrupted, the crucible is digested in water until the melt is dissolved, and after some further digestion the liquid is filtered and the residue washed; this residue should dissolve completely in hydrochloric acid unless quartz be present in the ore. The estimation of the chromium in the aqueous solution and washings is best performed by the addition of a known weight of ferrous sulphate to the acidified liquid and determining by standard dichromate the portion of this salt which remains unoxidised.

A. G. B.

Estimation of Sugar in Blood. By M. ABELES (*Zeit. physiol. Chem.*, **15**, 495—504).—The usual method of getting rid of the proteïds in the blood before estimating the sugar is either to boil with sodium sulphate and acetic acid (Bernard) or with sodium acetate and ferric chloride (Schmidt-Mulheim, Seegen). Schenk (this vol., p. 350) has stated that the former method leads to a considerable loss of sugar, although several other observers have found that the loss is not so great as Schenk states, and explain it in a different way. There are also objections to Schmidt-Mulheim's method which the present author has previously pointed out (*Wien. Med. Jahrb.*, 1887). He now recommends a new, simple, and efficacious method, and illustrates its accuracy by a table of analyses. The procedure is the following:—To the blood is added an equal volume of a solution of zinc acetate in absolute alcohol. The strength of this solution should be such that for each gram of blood 0·05 gram of zinc acetate is added. The precipitate is filtered off, squeezed, and washed with alcohol, the washings being added to the filtrate; to the latter a 20 per cent. solution of sodium carbonate is added until the reaction is strongly alkaline, and the precipitated zinc carbonate is filtered off. The filtrate is acidified with acetic acid and evaporated to 20—30 c.c. (50 c.c. of blood is usually taken). A few drops of a concentrated aqueous solution of zinc acetate is added, and then sodium carbonate until the mixture is alkaline; finally it is made up to the original volume and filtered, the sugar being estimated in this filtrate. Instead of zinc acetate, zinc chloride may be used.

W. D. H.

Estimation of Tannin and of Free Tartaric Acid in Wines. By A. VIGNA (*Staz. Sper. Agrar.*, **19**, 279—298).—The following modification of Löwenthal's method for the estimation of tannin is recommended:—50 c.c. of the tannin solution or the wine mixed with 5 c.c. of ammoniacal zinc acetate solution (zinc acetate, 40 grams; ammonia in excess, and the whole made up to 1 litre) is heated in a dish on a water-bath, being stirred from time to time, until the volume is reduced to about one-third; water (50 to 60 c.c.) is added, the whole mixed and allowed to get cool, when it is filtered, and the precipitate washed with cold water. The precipitate is at once dissolved in dilute sulphuric acid (1 : 4; 10 c.c.) and boiling water in the dish already used. When cold, 20 c.c. of indigo solution (1 gram to a litre) is added, the liquid diluted to about 250 c.c., and permanganate added until the colour of the indigo disappears. By using cold solutions of about 250 c.c., and by carefully adding the permanganate drop by drop, good results are obtained. A point of importance is that the amount of permanganate required is not always proportional to the tannin. Experiments made with tannin solutions containing respectively 1, 2, 3, and 4 parts per million showed that the amount of permanganate required is relatively greater the stronger the solution; thus, the amounts required by 50 c.c. of the above solutions were respectively 9·7, 20·5, 32·0, and 44·0 c.c. The difference is, however, not great enough to be of practical importance. The experiments show that the separation of tannin in wines by zinc acetate is sufficiently complete if too great an excess of zinc salt is avoided and the precipitate is rapidly washed and redissolved. Gannter's method is discussed, and is not recommended.

With regard to the estimation of free tartaric acid in wines, the methods of Berthelot and Fleurieu and of Barth, and the potassium chloride method, were tried. The direct determination with potassium acetate or chloride is the quickest, and gives results nearest the truth, especially when much acid is present. The addition of alcohol and ether may be omitted. The potassium chloride method is the simplest, and gives good results. N. H. M.

Detection of Sesame Oil in Olive Oil. By J. F. Tocher (*Pharm. J. Trans.*, **21**, 638—649).—A solution of pyrogallol in hydrochloric acid (2 grams in 30 c.c.) gives a reaction characteristic of sesame oil, after a sample of olive or other oil containing even a small proportion (1 per cent.) has been agitated with it. The hydrochloric acid solution, after having been separated from the oil, is boiled for five minutes, when the colour will be changed to purple, and the solution, after a time, will deposit a purple substance. The author also found that by agitation with acetic acid sesame oil yielded 0·04 per cent. of an extract which, by approximate treatment of the acid solution, was finally obtained in the form of fine, acicular crystals, melting at 117°, and soluble in alcohol and other solvents. It gave no reaction with the hydrochloric solution of pyrogallol, but by nitrosulphuric acid was turned first green, and then bright red, an effect which has been already observed with sesame oil itself, and used as a test. The percentage composition of the substance was found to be: C, 30·53; H, 5·43; O (by difference), 64·04. R. R.

Analysis of a Mixture of Wax, Paraffin, Stearin, and Stearic Acid. By F. Jean (*Bull. Soc. Chim.* [3], **5**, 3—5).—3 or 4 grams of the mixture are treated with 60 c.c. of boiling alcohol. On cooling, the alcoholic solution is titrated with seminormal alkali, phenolphthaleïn being used as an indicator, and the stearic acid is thus determined, since 7·8 c.c. of seminormal alkali = 1 gram of stearic acid. To the above neutralised alcoholic solution, 3—4 c.c. of sodium hydroxide solution (50 per cent.) is added, and the mixture is boiled in a reflux apparatus for one hour; the alcohol is now distilled off, and the residue is mixed with dry silica and asbestos, dried at 100°, and exhausted with hot chloroform; subsequent distillation of the chloroform leaves a residue of paraffin and myricic acid, which is weighed, and the paraffin is determined in a portion of this residue by heating it in a reflux apparatus with 4—5 c.c. of glacial acetic acid for one hour. The solution is now placed in a graduated tube, to which the rinsings of the flask with warm glacial acetic acid are added, and the tube and contents are placed in a water-bath at 90°, and frequently agitated. The volume of separated paraffin is read off and determined, since 1 gram of paraffin occupies under these conditions 1·35—1·4 c.c., and the myricic acid is taken by difference. The portion of the alcoholic residue which is insoluble in chloroform consists of sodium stearate, stearin, and cerotic acid. This is dissolved in boiling water, filtered from the silica and asbestos, and the solution decomposed by the addition of slight excess of nitric acid, the fatty acids are filtered off, and the filtrate is neutralised, treated with plumbic acetate, and the glycerol contained therein estimated by potassium dichromate; from the glycerol, the stearin is estimated on the assumption that 5 grams of glycerol are = 95 grams stearin, and the cerotic acid is taken by difference. T. G. N.

Estimation of Fats in Vaselin. By VIZERN and C. NICOLAS (*J. Pharm.* [5], **24**, 49—51).—Caustic alkalis are without action on the normal constituents of vaselin in the process to be described, whilst they combine in definite proportions with the fats to form soaps. Experiment has determined that 10 grams of these fatty compounds absorb 1·635 grams of potassium oxide, K_2O, and the calculations are based on this. A standard alkali solution is prepared by dissolving about 20 grams of potash in 100 c.c. of 90° alcohol. This is standardised by means of standard sulphuric acid. A neutral alcohol is prepared by dissolving 1 c.c. of phenolphthaleïn in 500 c.c. of 90° alcohol, then alkali is stirred in drop by drop until a very slight rose tint is produced. 10 grams of the vaselin to be tested is placed in a 200-c.c. porcelain basin, 10 c.c. of standard alkali added, the basin being kept on a water-bath during the whole process. 50 c.c. of neutral alcohol is now added, the solution heated nearly to boiling, and the mixture stirred for eight minutes, when the saponification will be complete, and normal sulphuric acid added drop by drop until *all colour has disappeared;* this point is very important. If too long a time has been taken, it may be necessary to add a fresh portion of neutral alcohol to replace the loss by evaporation. The amount of sulphuric acid run in subtracted from that required to saturate 10 c.c. of alkali solution, multiplied by 0·0047, gives the quantity of potash absorbed by the fats in 10 grams of vaselin, and this number divided by 0·01635 gives the percentage of fats in the vaselin. J. T.

Optical Analysis of Butter Fat. By H. O. G. ELLINGER (*J. pr. Chem.* [2], **44**, 157—159).—The author describes the testing of butter fat in the "difference refractometer" (this vol., p. 1305). He records the deflection given by 510 samples of pure Danish butter, taken with the view of ascertaining to what extent the refraction of pure butter fat varies, and therefore to what extent the refraction of butter can be used as a test for its purity. The readings were made at a temperature of 45°, and the "normal oil" of Amagat and Jean was used in the middle cell.

The samples were taken between February and June (209), during September and October (174), and in November (57) and December (70). The mean deflections for these four periods were 30·5, 27, 30·5, and 33 divisions respectively; the greatest deflection given by any sample was 37, and the least 23 divisions. Commercial margarin always contains some butter fat; the sample which contained least, in the author's experience, gave a deflection of eight divisions; when this sample was mixed with an equal quantity of butter of 35 deflection, the reading given by the mixture was 21·5, or 1·5 below the lowest natural butter (23).

The author concludes that natural butter gives a deflection varying between 35 and 23 divisions, and that the refractometer can only detect with certainty more than 45 per cent. of admixed margarin.

A. G. B.

Estimation of Fat in Milk. By M. KÜHN (*Chem. Centr.*, 1891, i, 1007; from *Milch. Zeit.*, **20**, 369—370).—For the estimation of fat in curdled milk, the author recommends Dietrich's method and weighing tubes.

The author also describes a small wire cage for holding the Adams' coils, which consists of two rings about 1 inch in diameter, into which the coil is slipped and weighed. The milk in then pipetted on to the coil, and the latter again weighed. J. W. L.

Estimation of the total Alkaloïds in Quinine Bark. By W. HAUBENSAK (*Chem. Centr.*, 1891, i, 1006—1007; from *Schweiz. Wochenschr. Pharm.*, **29**, 147—151).—The author recommends the following method for the estimation of the total alkaloïds in quinine bark in preference to that described in the *Pharm. Germ.* III; it differs from the latter in that the alkaloïds are extracted from the ether-alcohol ammonia solution by agitation with dilute sulphuric acid, by which means the alkaloïds are obtained free from resinous matters and wax.

20 grams of the finely-pulverised bark is shaken in a 500-c.c. flask with 10 c.c. of 10 per cent. ammonia and 20 c.c. of 94 per cent. alcohol; 170 c.c. of ether is added, and the whole shaken occasionally during 2—3 hours. 100 c.c. of the clear extract is poured off into a separating funnel, and shaken with 50 c.c. of water and so much sulphuric acid that the resulting liquid has a slightly acid reaction. The aqueous layer is allowed to separate from the ether, run off, warmed in order to expel the dissolved ether, and returned to the separating funnel; 30 c.c. of chloroform is then added, the alkaloïds liberated by the addition of a few drops of caustic soda solution, and, after shaking well, the chloroform

extract is separated, run into a tared flask, and the chloroform distilled off. The residue is dried at 100°, and weighed. The alkaline liquid, after separating the chloroform, is tested with iodine solution or Meyer's reagent, and should give no alkaloïd reaction; otherwise it must be again extracted with chloroform. The alkaloïd residue is obtained crystalline, more or less yellowish coloured, clear and completely soluble in acidified water. The process occupies 4—5 hours, and the results obtained are satisfactory. J. W. L.

Estimation of Caffeïne. By B. H. Paul (*Pharm. J. Trans.*, **21**, 882).—More caffeïne is obtained from a mixture of tea with magnesia when extracted with chloroform than from a mixture of tea with lime; but in each case this menstruum fails to dissolve out, even after prolonged treatment, more than a fraction (one-half, one-third) of the caffeïne actually present. Chloroform cannot therefore be substituted for alcohol in estimating the amount of caffeïne in tea, and its employment may account for the smallness of the amounts of caffeïne in tea that some analysts have reported. R. R.

Estimation of Morphine. By A. Lambert (*J. Pharm.* [5], **23**, 593—597).—It is known that the rotatory power of morphine in acid solution diminishes as the solution becomes more concentrated. If p represents in grams the quantity of morphine (supposed hydrated) contained in 100 c.c. of solution, $\alpha°$ the deviation produced in a column 0·2 m. long, then $p = 31 - \sqrt{961 - 25\alpha}$. It is found by calculation and verified by experiment that, to produce a deviation of 10° saccharimetric (or 2·167° of arc), it is necessary to dissolve 1 gram of morphine in 112 to 113 c.c. To estimate the morphine in opium, 15 grams is treated with 6 grams of slaked lime and 150 c.c. of water added in small portions; after stirring occasionally, the liquid is filtered off at the end of half an hour. To 53 c.c. of the filtrate is added 1 c.c. of acetic acid, 2 c.c. of water, 1 gram of powdered sodium sulphite, and some fragments of zinc. After a quarter of an hour the solution is filtered and examined in the polarimeter: let N be the deviation in degrees. 60 c.c. of the first solution is now actively shaken with 3·5 grams of ammonium chloride during 10 minutes, filtered, and 41 c.c. of the filtrate is treated with 1 c.c. of acetic acid, 0·75 gram of sodium sulphite, and some small fragments of zinc. After a quarter of an hour, it is filtered and examined in the polariscope; let n be the deviation, then $\mathrm{N}-n$ indicates the quantity of morphine contained in 100 parts of opium. J. T.

Optical Estimation of Albumin in Urine. By H. O. G. Ellinger (*J. pr. Chem.* [2], **44**, 256).—The author has employed Amagat and Jean's differential refractometer for the estimation of albumin in urine. A portion of the urine is boiled, after the addition of a drop of acetic acid, and the albumin removed; the filtrate is then made up to the original volume and introduced into the space bounded by the two parallel glass plates between the collimator and the telescope, whilst the original urine is put into the prism. If the zero of the instrument has been previously adjusted, the boundary line between light and dark falls the further to the right of the zero the more albumin the urine contains. The method gives results which are exact enough for practical purposes.

A. R. L.

Estimation of Caseïn in Milk. By J. Roux (*Chem. Centr.*, 1891, i, 1094—1095; from *Moniteur Scientif.* [4], **5**, 478—482).—The author recommends the following method, which is a modification of that of Adams, for the estimation of caseïn in milk; 10 c.c. of milk is extracted with 25 c.c. of the Adams' mixture of ether, alcohol, and ammonia, the aqueous layer is run off, the ether layer containing the fat is again washed with water, and the washings added to the aqueous layer, the volume of the whole now measuring 40—50 c.c. 2 c.c. of 50 per cent. trichloracetic acid is added, the liquid shaken, and the precipitated caseïn collected on a tared double filter. It is then washed with 50 c.c. of water containing 1 c.c. of trichloracetic acid, and the caseïn dried at 110°. If the milk should be curdled, it is well to shake it first with 1 or 2 c.c. of 25 per cent. ammonia, before extracting with the ether-alcohol mixture.

The filtrate from the caseïn does not react either with Esbach's or with Tanret's reagent, showing the absence of peptones, from which the author concludes that these compounds are either absent altogether, or present in fresh milk only in very small amount, since they are not precipitated by trichloracetic acid, and must, therefore, be in the filtrate from the caseïn. It is to be noted that the presence of trichloracetic acid can completely prevent the reduction of Fehling's solution by lactose.

J. W. L.

Estimation of Indigotin for Commercial Purposes. By F. A. Owen (*Chem. News*, **63**, 301—302; from *J. Amer. Chem. Soc.*, Jan., 1891).—The method, as previously described (Abstr., 1890, 96), has been considerably modified. Two lots, of 1 gram each, of coarsely powdered indigo shavings are taken: in one, the moisture and ash are determined; the other is first pulverised dry, then levigated with water, the suspended portion poured off, and the process repeated, until all is transferred to a 200-c.c. flask; 3 grams of zinc-dust and 60 c.c. of commercial strong ammonia are then added, the flask filled to $\frac{1}{2}$ c.c. above the mark, and shaken occasionally until reduction is complete (possibly from half an hour to two hours); 50 c.c. of the clear solution is then put in an evaporating basin, 5 or 6 drops of ether added, and air blown through to precipitate most of the indigotin; a moderate excess of hydrochloric acid is now added, the whole heated to boiling, and the precipitated indigotin collected on a tared filter, dried at 100°, and weighed.

D. A. L.

General and Physical Chemistry.

Copper Oxide Battery. By F. DE LALANDE (*Compt. rend.*, **112**, 1253—1256).—The element consists of one or more plates of zinc and a plate of agglomerated cupric oxide suspended in a 35 per cent. aqueous solution of potassium hydroxide. The zinc is supported by strips of amalgamated brass, and is completely immersed in the solution. The plates of copper oxide are prepared by subjecting a mixture of moist granular copper with 5 per cent. of clay to hydraulic pressure, and roasting the cakes at 600—700°, or by mixing the copper with 6 to 8 per cent. of tar and roasting in a reverberatory furnace. In order to give the requisite conductivity to the porous copper oxide, it is coated electrolytically with a very thin film of copper. The characteristics of this element are its low internal resistance, its great constancy, and its great yield of energy. The E.M.F. on open circuit is 0·94 volt. C. H. B.

Electromotive Forces of Polarisation. By M. LE BLANC (*Zeit. physikal. Chem.*, **8**, 299—330).—Starting with the assumption that electrolytes are present in a dissociated condition in aqueous solution, the author argues that the electrical energy required to separate the ions from the solution will be given by the product of the amounts of electricity peculiar to each ion into the intensities with which these amounts may be attached to the ions. The intensity of attachment will vary with the nature of the ion, but will always be the same for the same ion, provided that the influence which the solvent may be supposed to exercise on the dissolved substance remains constant. If the E.M.F. which is just sufficient to produce a separation of the ions from a solution of a given salt be accepted as a measure of the intensity of attachment of the electricity to the ions, constant differences might be looked for in the values of E.M.F. for salts having common ions.

The author has measured the above E.M.F. for normal solutions of a number of salts. The following table for salts of potassium and sodium shows that the constant differences predicted by the theory are actually obtained :—

		Diff.			Diff.
Na_2CO_3	= 1·71 volts		K_2CO_3	= 1·74 volts	
		0·44			0·43
$NaNO_3$	= 2·15 ,,		KNO_3	= 2·17 ,,	
		0·06			0·03
Na_2SO_4	= 2·21 ,,		K_2SO_4	= 2·20 ,,	
		0·23			0·24
NaCl	= 1·98 ,,		KCl	= 1·96 ,,	
		0·40			0·35
NaBr	= 1·58 ,,		KBr	= 1·61 ,,	
		0·46			0·47
NaI	= 1·12 ,,		KI	= 1·14 ,,	

Experiments with other salts serve to confirm the above results.

A number of sodium salts of organic acids were next examined, and it was found that all these gave about the same value, a value practically equal to that for the nitrate and sulphate. As it is improbable that the intensity of attachment is the same for the organic as for the inorganic acids, this number must be regarded as the maximum value which the E.M.F. can reach. The existence of such a maximum value can, however, only be explained by assuming that in these cases we are dealing, not with different processes, but always with one and the same process. This process the author believes to be the primary electrolysis of the water by the current. The maximum value is therefore the value for the decomposition of water. If this is the case, it will be necessary to assume that the water is in a partially dissociated condition, and the electrolysis of any given salt, such as potassium nitrate, would then take place as follows:—The conduction of the current would take place solely by the ions of the salt, but in the neighbourhood of the electrodes the potassium (positive) would form potassium hydroxide with the hydroxyl group (negative) of the water, the remaining hydrogen then giving up its charge at the electrode; the NO_3 ion (negative) would combine with the hydrogen (positive) of the water, and the remaining hydroxyl group would give up its charge at the electrode. The above hypothesis serves to explain a number of facts which have hitherto remained unexplained, as for instance the production of pure oxygen at the positive electrode in the electrolysis of acetic and benzoic acids in dilute solution. H. C.

Specific Heats of some Solutions. By W. TIMOFÉEFF (*Compt. rend.*, **112**, 1261—1263).—The author has determined the specific heats of solutions of mercuric chloride and cadmium iodide respectively in various proportions of methyl or ethyl alcohol. In all the solutions, the two salts have practically the same molecular capacity for heat, the mean value being 52. The specific heat in the case of methyl alcohol solutions is given with considerable accuracy by the formula $C = 0·56755 + 0·001633t$, and in the case of ethyl alcohol by the formula $C = 0·53574 + 0·002132t$.

The specific heat of cadmium iodide in concentrated aqueous solution is considerably lower than in alcoholic solution, whilst in dilute aqueous solutions it approaches that of the salt in the solid state.

C. H. B.

Heats of Neutralisation. By S. ARRHENIUS (*Zeit. physikal. Chem.*, **8**, 419—424).—E. Wiedemann has sought to explain, without the aid of electrolytic dissociation, the equality of the heats of neutralisation of strong acids by strong bases in dilute solution, on the assumption that, for example, (K, Cl) — (K, Br) = (H, Cl) — (H, Br), the salts being supposed to be solid, and the acids gaseous.

Arrhenius shows from thermochemical data, that this assumption is not justified for the undissociated substances, solids or gases. Of 179 combinations tabulated, only 12 fulfil the condition.

Arrhenius also corrects a misstatement of Wiedemann's regarding the heat of dissociation of water and its temperature coefficient.

J. W.

Calculation of the Boiling Point of a Liquid under any Pressure. By G. HINRICHS (*Zeit. physikal. Chem.*, **8**, 340—342).—

Against the logarithm of the pressure (p) in atmospheres as abscissa, the author tabulates the corresponding boiling point of a liquid as ordinate. A tangent to the curve thus obtained is drawn from the critical point (θ, π), and prolonged to cut the axis of abscissæ at the absolute zero in ζ_1 ($T = 0$, $\log p = \zeta_1$). If $\delta = \log p - \zeta_1$, then $Y_1 = K_1\delta$ (*Zeit. phys. Chem.*, **8**, 231). By subtracting Y_1 from observed values of T, Y_2 is obtained, and is equal to $K_2\Delta^2$, where $\Delta = \log \pi - \log p$. K_1 and K_2 are numbers which may be deduced from the curves, and once they are known, the boiling point in the absolute scale of temperature for any pressure may be calculated from the formula $T = K_1\delta + K_2\Delta^2$. The author gives some examples of the excellent agreement between observed and calculated values (for carbonic oxide, ammonia, and chlorine), but in the case of water doubts the accuracy of the critical constants determined by Dewar, as here the agreement is not satisfactory. J. W.

Vapour Density of Ammonium Chloride. By O. NEUBERG (*Ber.*, **24**, 2543—2544).—The author has determined the vapour density of ammonium chloride under reduced pressure in the apparatus recently described by himself and Lunge (this vol., p. 635). Under a pressure of 25 mm., the vapour density was found to be 1·13 and 1·2; under 46 mm. pressure in an atmosphere of hydrogen chloride, it rose to 1·5, and under 60 mm. pressure in ammonia, to 1·68 and 1·71. The vapour density of unaltered ammonium chloride would be 1·85, and in case of complete dissociation 0·925. These results show, therefore, conclusively that the molecule of ammonium chloride can exist in the gaseous condition.

Similar experiments with sulphur gave values which point to the existence of the molecule S_8. H. G. C.

Vapour Pressure of Water up to 200 Atmospheres. By C. ANTOINE (*Compt. rend.*, **113**, 328—331).—Cailletet and Colardeau give the following expression for the vapour pressure of water at any temperature t up to 325°, in atmospheres :—

$$t = \frac{1638 - 0{\cdot}0005P^2}{5{\cdot}0402 - \log P} - 225.$$

If the value of t is below 200°, the quantity $0{\cdot}0005P^2$ is practically so small that it may be neglected. The author calculates and tabulates the values for $0{\cdot}0005P^2$ above 200°, and also gives the values of P for every 10° from 220° to 360°. H. C.

A Theorem of Willard Gibbs. By P. DUHEM (*Zeit. physikal. Chem.*, **8**, 337—339).—Konovaloff has shown (*Ann. Phys. Chem.* [2], **14**, 34 and 219) that when a mixture of two volatile liquids has a greater (or smaller) vapour pressure than any other mixture of the same components, then the composition of the liquid is the same as that of the vapour. Gibbs has deduced this result on theoretical grounds, and the author now gives a detailed proof of the following general theorem: In a system of two coexisting phases, in order that the pressure should be a maximum (or a minimum) at constant temperature, or that the temperature should be a maximum (or a minimum) at constant pressure, it is necessary and sufficient that the two phases possess the same composition. J. W.

Calculation of Molecular Volumes. By G. HINRICHS (*Compt. rend.*, **113**, 36—38).—The author in this paper communicates two methods of arriving at the molecular volume of the members of homologous series. He first supposes that the normal paraffins have molecules composed of n similar joints (CH_2 groups), and terminated at each end by a hydrogen atom. The volume of C_nH_{2n+2} is thus $v_n = n \, . \, k + 2h$. The volume h is diminished by the mutual attraction of the molecules, and this diminution reaches a maximum when $n = v$ (here 15), h being then equal to h'. For $n < v$ we may thus write $h = h' + k'(v - n)^a$, and $v_n = nk + 2(h' + \epsilon)$, where $\epsilon = k'(v - n)^2$.

Taking the constants $k = 17{\cdot}8$, $h' = 3{\cdot}45$, $k' = 0{\cdot}1$, and $v = 15$, the accordance between theory and experiment is exceedingly good. The odd members of the series have in general values slightly below those calculated : the even members have values slightly in excess.

Another method is adopted in the case of the ethereal salts of the normal fatty acids, $C_qH_{2q-4}O_2C_pH_{2p+1}$. The molecule is here supposed to rotate on a longitudinal axis, and the oxygen atoms to determine the cross section of the solid of revolution. The author arrives at the formula $v_n = n \times 24{\cdot}6 + 2\epsilon$, where $p + q = n$, and $\epsilon = 1{\cdot}25(7 - n)$. J. W.

Capillarity Constants of Organic Substances in Aqueous Solution. By J. TRAUBE (*Annalen*, **265**, 27—55).—In investigating the subject of capillarity, the author and others have hitherto only paid attention to the capillarity constants a^2 and $\alpha (= \gamma)$, constants whose values are given by the capillarity equations $a^2 \cos \vartheta = rh$ and $\alpha \cos \vartheta = rhs/2$. It seemed desirable, therefore, to study the capillarity of molecular solutions and, by subtracting the constants of the solution from those of water, to obtain others which would show the influence of the nature, number, and size of the dissolved molecules. Such constants would be a measure of the capillary forces exerted by the molecules in solution, and, assuming that no dissociation or association phenomena accompany a change in concentration, it follows that the constants $a^2_W - a^2_1 = e^2$ and $\alpha_W - \alpha_1 = \epsilon$ (compare Abstr., 1885, 1033; 1887, 101) must increase proportionately with the concentration c, or, in other words, the products of concentration and capillarity, ce^2 and $c\epsilon$, must be constant. This being the case, it would follow that a law, corresponding with Boyle's law for gases, is also true for dilute solutions. As the concentration increases and the molecules coalesce to more complex aggregates, the values of ce^2 and $c\epsilon$ must decrease ; from the magnitude of this decrease, and by determining the concentration at which the above expressions become constant, conclusions not without an important bearing on the dissociation or association phenomena of solutions might probably be drawn. The constants ce^2 and $c\epsilon$, which correspond exactly with the values μ for the molecular conductivity, may be termed the specific and the actual molecular cohesion respectively.

The detailed results of the examination of solutions of a number of monocarboxylic acids, alcohols, and ethereal salts of the fatty series, and also of various other fatty substances (some of which are mentioned below) are given in tables.

From a study of these results, it is seen that the molecular cohesion $c\epsilon$ increases as the concentration decreases, until a constant end value is approximated; this approximation to a constant value takes place at different concentrations with different substances. It has been previously shown by Buliginski, Quincke, and Volckmann that the quotient of the values $c\epsilon$ for solutions of most salts is approximately equal to unity for the concentrations $c = 1$ to $c = \infty$; roughly speaking, this is also true as regards solutions of the compounds of the oxalic series, of acetamide, and of ethylene glycol, so that Boyle's law holds good to a certain extent even for high concentrations. In the case of the fatty, monohydric alcohols, monocarboxylic acids, and ethereal salts formed therefrom, a considerable degree of dilution must be attained, especially when the compound is rich in carbon, before the ratio of the values $c\epsilon$ approximates to unity; nevertheless, the values obtained experimentally with the monocarboxylic acids, allyl alcohol, butaldehyde, and hydroxyisobutyric acid indicate clearly that with sufficiently dilute solutions, Boyle's law would hold good.

On comparing the author's results with those obtained by Ostwald in his studies on electrical conductivity, it is seen that the influence of concentration is, on the whole, very much the same in both cases, and there can be little doubt that the decrease of conductivity and the decrease of molecular cohesion with increasing concentration are both due to the same cause. The analogy between electrical conductivity and capillarity is also shown by the fact that the higher the capillary activity of a substance is, the lower, in general, is the electrical conductivity of its solution. Salts are capillary inactive but electrolytically active; most, or many, organic compounds show the opposite behaviour. Generally speaking, the greater the capillarity of a solution the greater also the conductivity, although many organic substances form exceptions to this rule; even in such cases the entrance into a molecule of the most various groups and atoms, as, for example, CH_2, OH, H_2, Cl, C_6H_5, affects the two constants in a similar manner, and it is quite evident that the same assumption which is made to explain the change in electrical conductivity with a change in concentration must also be made in the case of capillarity.

The association hypothesis put forward by the author (*Ber.*, **23**, 3582; compare this vol., p. 390) accounts for this change by assuming that as the concentration increases the molecules coalesce to form more complex aggregates; the following considerations will show that the capillarity constants afford a means by which these association phenomena may be determined numerically:—

(1.) In homologous series of capillary active substances, the (approximately) constant end values of the molecular cohesions for sufficiently dilute solutions are in the ratio $1 : 3 : 3^2 : 3^3$ . . . , or, in other words, the pressure which the dissolved molecules exert on unit of surface increases in homologous series of capillary active substances by the addition of CH_2 in the ratio $1 : 3 : 3^2 : 3^3 \ldots$; this rule does not hold good in the case of members of the oxalic series, but only for capillary active substances.

If, by graphic interpolation, the concentrations corresponding with equal capillary pressure, that is to say, for isocapillary solutions, are calculated, conclusions of very considerable importance for the association theory can be arrived at, and, neglecting certain irregularities which are most evident at high concentrations, the following rules may be laid down. (2.) In homologous series of capillary active substances, the proportion between the number of molecules which exert equal pressure on the unit of surface is constant and almost independent of the number of the dissolved molecules. (3.) In isocapillary solutions of substances differing by nCH_2, the proportion between the number of molecules of the dissolved substances is as $1 : 3^n$.

Now if it be granted that, with increasing concentration, the molecules become associated to form larger aggregates, the fact that the law (1) stated above holds good even for high concentrations can hardly be accounted for except by the further assumption that, in such isocapillary solutions of homologous substances the association of molecules to aggregates is proportional to the number of simple molecules in solution; that is to say, the proportion between the more complex aggregates is the same as that between the simple molecules.

Assuming, again, the truth of the association hypothesis, it would seem, from the results obtained with solutions of high concentration that, with increasing concentration, the association of the molecules takes place proportionately to the number of the dissolved molecules.

In addition to the above statements, the following facts may be quoted as showing the relation between capillarity and constitution. The capillary constants of solutions of fatty acids are practically the same as those of the fatty ethereal salts with which they are metameric; propionic acid, for example, gives approximately the same values as methyl acetate, propyl formate the same as those of methyl propionate. Nevertheless, in the case of many isomerides, the arrangement of the atoms is not without influence, even in dilute solutions; although solutions of the two propyl alcohols, for example, and of the two butyric acids, have practically the same capillarity, this is not so in the case of isoamyl alcohol and its isomeride dimethylethyl carbinol.

In isocapillary solutions of propyl acetate and allyl acetate, the ratio between the number of dissolved molecules is 1 : 2; this is also the case with solutions of the corresponding alcohols and amines, with dilute solutions of butaldehyde and isobutyl alcohol, propyl alcohol and acetone, succinic acid and maleïc acid—compounds which differ from one another by 2 atoms of hydrogen. Ethylene glycol, although richer in hydrogen than acetic acid, has a considerably greater capillary constant.

The entrance of a hydroxyl group into a molecule always increases the capillarity, but by a different amount in different cases. The entrance of a carbon atom into the molecule of a capillary active substance always diminishes the capillarity; the capillarity of butyric acid, for example, is to that of allyl acetate as 1 : 1·6 to 1·7, and the same is true as regards alcohol (or acetone) and allyl alcohol; in the case of propionic acid and butaldehyde, the ratio is 1 : 2, but the value of e^2 for propionic acid is about 1/20 of that of ethylene glycol, and a similar irregularity is observed in the ratio of the values for maleïc and malonic acids. F. S. K.

Determination of Molecular Weight at the Critical Point. By P. A. Guye (*Compt. rend.*, **112**, 1257—1258).—If π, θ, and ϕ are respectively the pressure in atmospheres, the absolute temperature, and the volume of a weight p of a compound at the critical point, then the critical density with reference to air at 0° and 1 atmosphere is

$$d = \frac{p\theta}{F\phi\pi \; 273 \times 0{\cdot}001293}.$$

d should be equal to the molecular weight divided by 28·87. F is a factor, having approximately the value 2·67, but this approximation is not sufficiently close. The author finds that it may be regarded as a linear function of the absolute critical temperature of the particular compound. Thus, $F = A\,(1 + B\theta)$. The numerical values of A and B as determined by means of the data for nitrogen (Sarrau) and iodobenzene (Young) are respectively 2·648 and 0·0009345. The first equation then becomes

$$d = 1146 \frac{\delta\theta}{\pi(1070 + \theta)},$$

δ being the critical density with respect to water or the weight of the substance ocupying a volume of 1 c.c. at the critical point.

The values obtained for hydrogen, ethylene, carbonic anhydride, sulphurous anhydride, ethyl alcohol, normal propyl alcohol, chlorobenzene, and iodobenzene by means of this equation are identical with the theoretical densities. C. H. B.

Cryoscopic Observations. By A. van Bijlert (*Zeit. physikal. Chem.*, **8**, 343—366).—Van't Hoff (Abstr., 1890, 1044) accounted for the abnormally small depression of the freezing point exhibited by some solutions on the assumption of the solid which separates on congelation not being the pure solvent, but an isomorphous mixture containing a quantity of the dissolved substance. The author has put this explanation to an experimental proof, and has investigated the following solutions; thiophen in benzene, metacresol in phenol, antimony in tin, and β-naphthol in naphthalene. The quantity of solution adhering to the crystals was estimated from special experiments with the solution to be examined and a third substance which did not crystallise out with the solvent.

In the case of thiophen dissolved in benzene, the author found, in five experiments with solutions of different concentrations, that the ratio of the thiophen in the crystals to that in the mother liquor was 0·41, 0·44, 0·17, 0·14, 0·14. The last three numbers were obtained from the most successful experiments, so the author concludes that on the partial congelation of thiophen-benzene solution, there is a crystallisation of thiophen to the extent of about 10 per cent. of that originally contained in the solution.

Although solutions of metacresol in phenol have an abnormally high freezing point, the author was unable to show by the method he adopted that any of the dissolved substance crystallised along with the solvent.

With antimony dissolved in tin, and β-naphthol in naphthalene, there is actually an elevation of the freezing point instead of a depression. This is accounted for by the solid which crystallises containing more dissolved substance than the solution itself. The following numbers were found :—

	Antimony, per cent.	β-naphthol, per cent.
Original solution........	5·0	9·1
Mother liquor	4·7	8·5
Crystals................	6·3	11·5

J. W.

Solution. By J. A. Wanklyn and W. J. Cooper (*Chem. News*, **64**, 27—28).—The authors have made observations from which they conclude that solution is simple and regular except where influenced by chemical action. There is no change in volume or temperature when sugar is dissolved in water, the volume of the solution being equal to the sum of the volumes of sugar and water; for every gram of sugar entering into 100 c.c. of the solution, a regular rise of 0·00371 in the specific gravity is observed.

A contraction of 9 c.c. occurs when 73·7 grams of sodium chloride is dissolved in a quantity of water equal to 500 c.c. less the volume of the salt taken; the solution obtained has a specific gravity of 1·0988; the increment for each gram of salt per 100 c.c. of solution being 0·00670, this number increases to 0·00709 in a solution containing 1·474 grams of salt. Sodium bromide or iodide shows less contraction and less variation in the increased gravity than in the case of the chloride; the number for the bromide is 0·00741 for 50·2 and 0·00757 for 10·04 grams per 100 c.c. of solution, whilst for the iodide the numbers are 0·00737 for 41·01 and 0·00747 for 8·202 grams per 100 c.c. of solution. Anhydrous barium chloride dissolves with development of heat; an 18·372 gram solution shows an increase in specific gravity equal to 0·00795 for each gram of the salt, whilst each gram of anhydrous calcium chloride showed an increase of 0·00675. A solution containing 62·1 grams of $MgSO_4,7H_2O$ in 100 c.c. had a sp. gr. of 1·271.

D. A. L.

Nature of Colloïdal Solutions. By C. Barus and E. A. Schneider (*Zeit. physikal. Chem.*, 8, 278—298).—A study of the properties of colloïdal solutions leads to the conclusion that such solutions consist of very finely divided matter which is held in suspension in the solvent. In order to obtain evidence as to the correctness of the above view, the authors have examined the behaviour of colloïdal silver solutions. Silver being an excellent conductor of electricity, a measurement of the resistance of such solutions should aid in determining whether the silver particles are held mechanically in suspension in the solution, or are present as molecules in the dissolved state. In the first case the liquid would be a non-conductor, in the second metallic conductivity might be expected. The experiments show that colloïdal silver, either in the solution or in the solid condition, is a non-conductor. These results, taken in conjunction with the other properties of colloïdal solutions, confirm therefore the views expressed above as to the nature of such solutions. H. C.

Action between Oxides and Hydroxides of Heavy Metals and the Halogen Compounds of the Alkalis. By W. Bersch (*Zeit. physikal. Chem.*, **8**, 383—395).—A solution of potassium chloride reacts with mercuric oxide until a state of equilibrium is reached between these two substances and the mercuric chloride and potassium hydroxide formed. Such reactions have been investigated by the author with regard to the amount of alkali liberated at different temperatures. On the one hand, he used the oxides of mercury, cadmium, and lead; on the other, the chlorides, bromides, iodides, and thiocyanates of the alkalis and alkaline earths.

He sums up his results as follows :—

1. Some oxides (hydroxides) of heavy metals are capable of decomposing halogen compounds of the alkalis with formation of free alkali.

2. If the metal forms an insoluble compound with the halogen, then, if excess of oxide be present, all the halogen is abstracted from the solution.

3. If the compound of the halogen with the heavy metal is soluble, a state of equilibrium is finally reached.

4. This is dependent on the degree of dissociation of the dissolved substance. The more it is dissociated, the less is the amount of free alkali.

5. The state of equilibrium is influenced by the heat of reaction. If heat is absorbed, the quantity of free alkali increases with rise of temperature and *vice versâ*.

6. The time required to reach the final equilibrium is dependent on the halogen; it is smallest with the iodides, and diminishes as the temperature is raised.

7. The amount of decomposition is dependent only on the halogen. The alkali metal with which the halogen is combined has very little influence in the reaction. J. W.

Velocity Coefficients of Bases. By S. Bugarszky (*Zeit. physikal. Chem.*, **8**, 398—418).—The author measured the rate at which various alkalis saponified methyl acetate, and calculated from his data the coefficient of velocity in each case in absolute (C.G.S.) units. The following table contains his results :—

Velocity Coefficients.

	Dilution in litres.			
	20.	40.	80.	100.
KOH	132·9	129·2	—	—
LiOH	129·8	—	—	—
NaOH	127·2	126·4	124·1	—
$Ba(OH)_2$	124·6	125·7	126·9	—
$Sr(OH)_2$	—	121·6	—	—
$Ca(OH)_2$	—	121·2	126·1	126·4

A comparison of conductivities (Ostwald, *J. pr. Chem.* [2], **33**, 352) with velocity coefficients gives:—

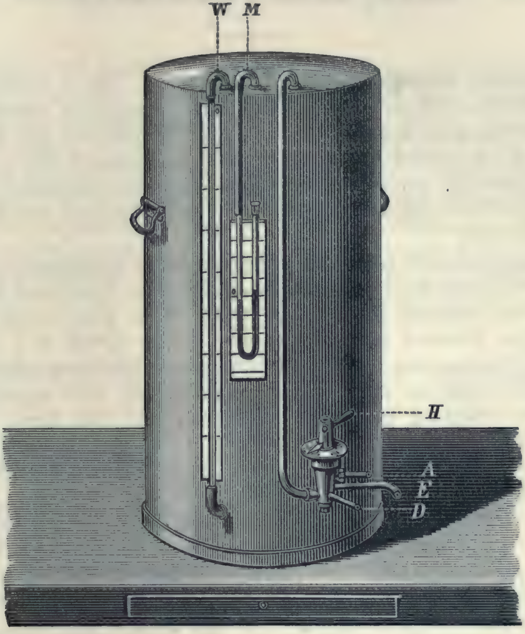
Base.	Electrical conductivity. KOH = 1.	Velocity coefficient. KOH = 1.
KOH	1·000	1·000
NaOH	0·930	0·965
LiOH	0·888	0·972
$Ba(OH)_2$	0·943	0·944
$Sr(OH)_2$	0·911	0·915
$Ca(OH)_2$	0·897	0·911

The temperature of experiment was 19·4°. J. W.

Energy Content in Chemistry and Physics. By F. WALD (*Zeit. physikal. Chem.*, **8**, 272—277).—A criticism of a former paper by Meyerhoffer (this vol., p. 975). The author objects to the method of decomposing energy into the two factors of content and potential, as not applicable to all forms of energy. The assumptions made in the thermodynamical portion of Meyerhoffer's paper are also shown to be untenable. H. C.

Glass Air Pump. By M. STUHL (*Ber.*, **24**, 2542—2543).—The author describes an air pump, made solely of glass, which may be used either for exhausting or compressing, and only requires a water pressure of 1 atmosphere to work efficiently. For details of construction, reference may be made to the sketch in the original paper. H. G. C.

Universal Gasholder. By EICHHORN (*Zeit. anal. Chem.*, **30**, 446—450).—The special feature of this gasholder is a tap, H (the construction of which is not described), which can be adjusted to five different positions. The nozzle A is to be permanently connected to a water supply giving a pressure of at least 1 metre of water. In position *a* of the tap, both inlet and outlet are closed; in position *b*, water can enter and compress the gas; in position *c*, water enters whilst gas issues at the nozzle D; in position *d*, the gas way is open, but that for water closed; and in position *e*, water escapes at E, while gas enters at D. The apparatus can therefore be used either to supply gas under pressure, or as an aspirator, in which latter case



E should be furnished with a long fall tube. Other patterns are constructed in which the tap H may be near the top of the gas holder, or even at a distance from it. M. J. S.

Lecture Experiment to Demonstrate the Dissociation of Ammonium Chloride. By R. Blochmann and R. Blochmann (*Ber.*, **24**, 2765—2766).—A hard glass tube, 120—150 mm. in length and 8—9 mm. in internal diameter, is sealed at one end, and held with the open end uppermost in a perpendicular position by a clamp; a piece of wire gauze, 10 cm. square, having a hole in the centre of such a diameter that it fits the tube tightly, is pushed towards the upper end of the tube as far as the clamp, its object being to protect this portion of the tube from the heating. A small quantity of ammonium chloride (about 0·05 gram) is now introduced, and the lower end of the tube heated with the full flame of a Bunsen's burner in such a manner that the point of the inner zone of the flame lies in the same horizontal plane as the bottom of the tube. If a piece of red litmus paper, moistened with water, be placed within the open end, it becomes blue after about a minute; this may be repeated two or three times, until at length the alkaline reaction is no longer observable; on now applying blue litmus paper, this soon becomes red. A. R. L.

Inorganic Chemistry.

Gravimetric Composition of the Air. By A. LEDUC (*Compt. rend.*, **113**, 129—132).—The author has previously shown that the gravimetric composition of the air, as determined by Dumas and Boussingault, does not agree with that calculated from Regnault's values for the sp. gr. of oxygen and nitrogen respectively (Abstr., 1890, 1370). The author has made new experiments, using Brunner's method.

Long, thin sticks of pure phosphorus were introduced into a glass flask of 2—3 litres capacity, and the flask was rendered vacuous and weighed, the residual pressure having been previously measured. Air was then allowed to enter slowly, being dried and purified by passing over potassium hydroxide and phosphoric anhydride. After 24 hours the balloon was again weighed. It was again rendered vacuous, the residual pressure measured, and the flask afterwards weighed. The difference between the first and second weighings gives the total weight of the air, and the difference between the first and third weighings gives the weight of the oxygen. Great care was taken to allow the flask to attain a state of equilibrium before making the weighings, and corrections were made for the difference in residual pressure, the contraction of the flask when made vacuous, and the small quantity of gas in the tube of the stop-cock. Two experiments gave respectively 23·244 and 23·203 per cent. of oxygen, the mean being 23·23. C. H. B.

Specific Gravities of Oxygen, Hydrogen, and Nitrogen. By A. LEDUC (*Compt. rend.*, **113**, 186—189).—The author has redetermined the relative densities of hydrogen, oxygen, and nitrogen, using a glass flask furnished with a glass stop-cock and an improved manometer, and taking special precautions to prevent errors from the wiping of the flask, &c. Correction was also made for the contraction of the flask when rendered vacuous. The results obtained are as follows:—

	Density. Air = 1.	Weight of 1000 c.c.
Hydrogen......	0·0695	0·08984
Oxygen........	1·1050	—
Nitrogen.......	0·9720	—
Air............	1·0000	1·2633

The composition of air, calculated from the sp. gr. of its constituents, is oxygen 23·235 per cent. by weight, and 21·026 per cent. by volume, results which agree well with those determined directly.

Regnault's result for the weight of a litre of air, when corrected for the contraction of the flask, is 1·2934, but the separate determinations are less concordant than those of the author (compare preceding abstract). C. H. B.

A Property of Sulphur. By C. Lepierre (*Bull. Soc. Chim.* [3], **5**, 308).—When fused sulphur, at 115° or thereabouts, is poured on a printed surface, on cooling, the impression is found imprinted on the surface of the sulphur which has been in contact therewith.

T. G. N.

Purification of Carbon Bisulphide. By A. Chenevier (*Chem. Centr.*, 1891, ii, 148; from *L'Union pharm.*, **33**, 204).—The unpleasant odour of carbon bisulphide may be entirely removed by the following process:—To 1 litre of carbon bisulphide, 0·5 c.c. of bromine is added and allowed to remain for 3—4 hours. The bromine is then separated again by shaking the carbon bisulphide with a slight excess of potash, or by means of copper turnings. The carbon bisulphide may now be opalescent, but this is readily removed by agitating it with a little potassium chloride, when the filtered bisulphide will be obtained clear, colourless, and of agreeable odour. It leaves no residue on evaporation.

J. W. L.

Isomorphism of Sulphur, Selenium, and Tellurium. By W. Muthmann (*Zeit. physikal. Chem.*, **8**, 396—397).—With reference to Retgers' suggestion (this vol., p. 1152), that tellurium is not isomorphous with sulphur and selenium, but rather with the platinum metals, the author points out that metallic tellurium is isomorphous with one form of selenium, and thinks the coincidence of form with osmiridium, etc., fortuitous.

J. W.

Phosphorus Trifluorodichloride. By C. Poulenc (*Compt. rend.*, **113**, 75—78).—Two half-litre flasks, provided with leading tubes from the upper and lower parts, and filled with chlorine and phosphorus trifluoride respectively, are connected in such manner that the fluoride can be displaced by mercury into the upper part of the chlorine flask. The gases contract to half their original volume, according to the equation $PF_3 + Cl_2 = PF_3Cl_2$, so that the operation is complete when the whole of the fluoride has been transferred. The mixture is left alone for some days; it must not be shaken with mercury, as it is slowly attacked by it even in the cold.

Phosphorus trifluorodichloride thus prepared is a colourless, uninflammable gas, having a sharp, irritating odour. It is instantaneously absorbed and decomposed by water and alkalis. Its vapour density is 5·40, the theoretical number being 5·46. It liquefies under ordinary pressure at −8°. It is decomposed by heat (250°) or electric sparks into phosphorus pentafluoride and pentachloride. Sulphur acts on it at 115°, forming sulphur chloride, and a new gaseous compound, *phosphorus sulphofluoride*, PF_3S, which has a disagreeable odour, is rapidly absorbed by alkalis, and in contact with water, splits up quantitatively into hydrogen phosphate, fluoride, and sulphide. When phosphorus is heated with the fluorochloride at 120°, it decomposes it, forming phosphorus trifluoride and trichloride. It is entirely absorbed by sodium. Magnesium, aluminium, iron, nickel, lead, tin, and mercury attack it at 180°, forming metallic chlorides, and liberating phosphorus trifluoride. Water in small quantity decomposes it, according to the equation $PF_3Cl_2 + H_2O = PF_3O + 2HCl$; if a larger quantity is used, the oxyfluoride is decomposed, according to the equation $PF_3O + 3H_2O = H_3PO_4 + 3HF$. Ammonia reacts with it to form *fluorophosphamide*, $PF_3(NH_2)_2$, a light, white solid, soluble in water. JN. W.

Arsenious Oxide Solutions. By E. G. CLAYTON (*Chem. News*, **64**, 27).—By agitating arsenious oxide with water at 15° at intervals of half an hour for 4 hours, at intervals of 20 minutes for 6 hours, or at frequent intervals during 4 days, solutions containing respectively 0·118, 0·269 (sp. gr. 1·0023), or 0·99 per cent. of the oxide were obtained. A solution containing 2·22 per cent. was obtained by boiling the oxide with water for an hour and leaving the mixture for 29 hours, but by continuing the boiling for 4 hours the solution at 93° contained 9·52 per cent., and on cooling, after 1½ hours, 8·24 per cent.; after 45½ hours, 3·28 per cent. (sp. gr. 1·0254); after 90 hours, 3·21 per cent., the arsenious oxide being deposited in a finely-divided, crystalline state. Boiling arsenious oxide with 10 per cent. aqueous potassium hydroxide for 3 hours yielded a hot solution containing 34·08 per cent., which, in 24 hours, had deposited crystalline arsenious oxide, retaining 14·29 per cent. in solution. D. A. L.

Boron Phosphide. By A. BESSON (*Compt. rend.*, **113**, 78—80).—Boron bromide unites with hydrogen phosphide at ordinary temperatures to form a light, white, amorphous solid, having the composition BBr_3,PH_3. This substance fumes abundantly in the presence of moisture, is violently decomposed by water, with evolution of hydrogen phosphide, and ignites spontaneously in air. It can be sublimed in a closed vessel, or in a current of inert gas, and condenses in small, highly refractive crystals. At 300°, it splits up into hydrogen bromide and boron phosphide, thus giving a convenient way of preparing the latter substance.

Boron phosphide thus obtained is a brown solid, insoluble in water, but soluble in boiling concentrated alkalis, with evolution of hydrogen phosphide. It burns in air, takes fire when projected into cold chlorine, and is attacked by bromine and iodine vapour; strong nitric acid destroys it, the mass becoming incandescent, and even the dilute acid dissolves it with avidity. It gives off hydrogen phosphide, when heated with soda-lime, and phosphorus, when raised to a red heat in a current of hydrogen; in the latter case the residue contains both phosphorus and boron, which seems to point to the existence of a second, more stable combination of these elements. When heated to redness in a stream of nitrogen, boron phosphide gives off phosphorus, and apparently absorbs nitrogen, for when the residue is heated with soda-lime, ammonia, as well as hydrogen phosphide, is obtained.

JN. W.

Silicon Chloriodides. By A. BESSON (*Compt. rend.*, **112**, 1314—1316).—The three silicon chloriodides are formed when vapour of iodine chloride is passed over crystallised silicon heated nearly to redness. $SiCl_3I$ boils at 113—114°; $SiCl_2I_2$ boils at 172°; and

$SiClI_3$ melts at 2°, boils at 234—237°, and rapidly becomes coloured when exposed to the air.

Iodine bromide seems to yield silicon bromiodides under similar conditions, but a large quantity of iodine is set free.

Sulphur chloride under similar conditions yields silicon chloride and free sulphur, but at a bright-red heat silicon chlorosulphides are formed; these are under investigation. C. H. B.

Silicon Bromiodides. By A. Besson (*Compt. rend.*, **112**, 1447—1449).—Silicobromoform, when heated in a sealed tube at 200—250° with iodine, yields the bromiodide $SiIBr_3$; a small quantity of higher substitution products is formed at the same time.

Dry hydriodic acid acts on silicon bromide at a little below a red heat, giving substitution products, the main constituent being $SiIBr_3$; the yield is small.

Bromine moniodide, when distilled over crystalline silicon, maintained at nearly a red heat, yields the three possible bromiodides, together with some silicon bromide and iodide. The product may be decolorised by fractionation over copper. The separation of the bromiodides is very difficult. Silicon bromiodides colour rapidly in the air; they absorb dry ammonia gas with the production of white, solid compounds decomposed by water. Silicon bromide in which much iodine has been dissolved may be used in place of the iodine bromide; with the chloride, no reaction occurs.

The bromiodide $SiIBr_3$ is a colourless liquid, distilling at 192°; it may be cooled to $-20°$ without solidifying, but, when solid, melts at 14°. The bromiodide SiI_2Br_2 is a white solid, which melts at about 38°, and distils at 230—231°. The remaining compound, SiI_3Br, is also a white solid, melts at 53°, and distils at 255°; it is difficult to separate from silicon iodide. W. T.

Silicon Selenide. By P. Sabatier (*Compt. rend.*, **113**, 132—133).—When crystallised silicon is heated to redness in a current of dry hydrogen selenide, it is converted into silicon selenide, without incandescence, at a temperature below the boiling point of selenium. The selenide has the composition $SiSe_2$, and, after fusion, is a hard, lustrous mass, of semi-metallic appearance. Cold water decomposes it with evolution of hydrogen selenide and separation of silica, but after a time decomposition slackens, and, although it is accelerated on warming, the silicon selenide is never completely decomposed, probably because it is protected by the silica that separates. With potassium hydroxide solution, which dissolves both the hydrogen selenide and the silica, decomposition becomes complete after some time. Aqua regia acts gradually on the selenide with separation of hydrated silica. Under ordinary conditions, silicon selenide evolves a very irritating odour, due, doubtless, to the hydrogen selenide formed by the action of the moisture in the atmosphere. At a red heat in a current of air or dry oxygen, the selenide is converted into silica, selenious anhydride, and selenium. C. H. B.

Carbon Tetriodide. By H. MOISSAN (*Compt. rend.*, **113**, 19—22). —Carbon tetrachloride reacts with boron iodide, BI_3 (this vol., p. 979), to form carbon tetriodide and boron chloride. The tetrachloride, which should be free from chloroform to avoid the formation of iodoform, is best heated in excess with crystals of boron iodide in a sealed tube at 90° for an hour; the tetriodide separates after a time in theoretical quantity, forming fine crystals, which, after washing with sodium hydrogen sulphite solution to remove adherent traces of iodine, are red in colour, and after slow sublimation in a vacuum at 100°, resemble artificial rubies in lustre and shade.

Heated at 140° in a current of hydrogen, carbon tetriodide is reduced to iodoform. It is attacked by chlorine, with the formation of carbon tetrachloride and the chlorides of iodine. Warmed gently in dry oxygen, it is decomposed into iodine and carbon. It reacts violently with fused sulphur, iodine and carbon being set free, and an unspecified compound of sulphur and iodine being formed; if, however, it is heated to 50° with powdered sulphur, carbon bisulphide and sulphur iodide are produced. Phosphorus acts energetically on it. When ground in a mortar with potassium or sodium, the mass becomes incandescent, carbon is liberated, and the alkali iodide is formed; mercury and powdered silver also attack it. Heated with water at 50°, in a sealed tube from which the air has been removed, it slowly decomposes. Hydrogen chloride and iodide have no action on it in the cold, but when heated with it, reduce it to iodoform and liberate iodine. JN. W.

Action of Light on Silver Chloride. By GUNTZ (*Compt. rend.*, **113**, 72—75; compare Hitchcock, Abstr., 1890, 213; this vol., p. 1155; Richardson, Trans., 1891, 536).—When silver chloride, spread in thin layers upon glass slips, is exposed to light, there is at first no darkening or loss of weight, but if it is treated at this stage with a photographic developer, such as ferrous oxalate, it is reduced to the metallic state, showing that a modification has taken place in its constitution. A similar modification is stated to be brought about by boiling silver chloride with water in a reflux apparatus in the dark for some hours.

The disengagement of chlorine may be rendered evident by concentrating a beam of sunlight on the chloride. The residual product in the early stages of the action is stated to be silver subchloride, Ag_2Cl, identical with that prepared from the subfluoride; if treated with ammonia or potassium cyanide, metallic silver is left, but dilute nitric acid does not dissolve it. The author states that he has found that the formation of this subchloride from the chloride is attended with absorption of heat = 28·7 cal., and considers that this explains the increased rapidity of the action when substances capable of absorbing chlorine and giving up heat are present. Silver subchloride, prepared in either of the above ways, is decomposed by the further action of light into silver and chlorine.

Since both the metal and its subchloride are opaque, the final product of the action of light on a layer of silver chloride usually consists of an upper layer of metallic silver, an intermediate layer of subchloride, and a lower layer of unchanged chloride. JN. W.

Silver Fluoride. By H. Moissan (*Bull. Soc. Chim.* [3], 5, 456—458).—A solution of well-washed silver carbonate in hydrofluoric acid is evaporated to dryness, with constant stirring, in a platinum basin, and the resulting black, pulverulent mass is dissolved in water and filtered. The clear filtrate, which, when left in contact with silver foil, yields crystalline silver subfluoride (compare Abstr., 1890, 1055), is evaporated in the dark in a vacuum over sulphuric acid. As thus obtained, silver fluoride forms a yellow, transparent, tough, elastic mass, which is soluble in water, and melts at a dull-red heat (the temperature as determined by Le Chatelier's thermo-electric method is 435°). Silver fluoride reacts violently with the chlorides of phosphorus, silicon, and boron, and with phosphorus oxychloride, yielding the corresponding fluorine compounds of the non-metal and silver chloride. T. G. N.

Electrolysis of Barium Chloride. By C. Limb (*Compt. rend.*, **112**, 1434—1436).—The author has been unable to obtain metallic barium by the electrolysis of fused pure barium chloride or of its admixture with sodium chloride.

The electrolyte was contained in a crucible of 500—600 c.c. capacity and a current passed from a small dynamo arranged to maintain a constant difference of potential of 10 volts. The anode consisted of a carbon plate, 5 cm. in length, and was separated by a bottomless, porous cylinder from a wrought iron cathode. The current passing at first was about 30 ampères; with the pure salt, this quickly fell to 2 or 3 ampères, but the original strength was soon regained on agitating the cathode; with the mixture, the electrolysis was regular. In both cases there was an abundant evolution of chlorine. The cathode, when plunged into water, only in a single case gave off a bubble of hydrogen when, according to Faraday's law, there should have been 260 grams of metal. The infusible, non-conducting deposit on the cathode was found to contain considerably less chlorine than the amount required by the barium and sodium present to form normal chlorides, when due allowance had been made for a certain amount of free barium oxide. The conclusion was therefore drawn that some subchloride of barium was formed. W. T.

Hardening of Plaster Casts. By M. Dennstedt (*Ber.*, **24**, 2557—2558).—The method consists in soaking the cast in a solution of silicic acid prepared by means of a dialyser, drying in a warm place, and then soaking in a solution of barium hydroxide at 60—70°, and again drying. A hard, compact casting is also obtained by mixing the plaster of Paris with aluminium or zinc hydroxide before casting and afterwards soaking in silicic acid. E. C. R.

Preparation of Crystalline Monocalcium Phosphate. By G. Pointet (*Bull. Soc. Chim.* [3], **5**, 254—256).—Neither the crystalline nor the honey-like commercial variety of monocalcium phosphate corresponds with the formula $CaH_4(PO_4)_2$, owing to the free sulphuric acid in the crude liquor acting on the phosphate during evaporation. By leaving tricalcium phosphate in contact with a solution of the honey-like commercial variety for some time, a solution is obtained which, on gentle evaporation, yields crystals of pure monocalcium phosphate. T. G. N.

Action of Acetates on Monocalcium Phosphate. By H. CAUSSE (*Bull. Soc. Chim.* [3], **5**, 298).—If monocalcium phosphate (50 grams) is dissolved in water, and glacial acetic acid (25 grams) added to the filtered solution, the subsequent addition of a few c.c. of an alkali acetate solution causes a turbidity, and the deposition after some days of rhomboidal scales of dicalcium phosphate of the formula $CaHPO_4 + 2H_2O$. Similar crystals are obtained when cold saturated solutions of sodium phosphate (1500 c.c.) and calcium chloride (400 c.c.) are mixed with fuming hydrochloric acid (100 c.c.), and a few drops of potassium acetate solution added to the mixture.

T. G. N.

Thallium Compounds. By C. LEPIERRE and M. LACHAUD (*Compt. rend.*, **113**, 196—198).—A boiling solution of 112 grams of potassium hydroxide per litre can dissolve about 3·5 grams of thallium chromate, which separates on cooling in hexagonal prisms, terminated by hexagonal pyramids. These crystals belong to the rhombic system, so that thallium chromate is isomorphous with potassium sulphate. No basic thallium chromates are obtained similar to those formed by lead chromate.

When thallium chromate is projected into fused potassium hydroxide, soluble potassium chromite, $Cr_2O_3,3K_2O$, and insoluble thallic oxide are formed. The latter remains in the form of hexagonal plates when the product is treated with water; sp. gr. = 5·56. It is insoluble in water, and dissolves with difficulty in sulphuric acid but more readily in hydrochloric acid.

If thallium chromate is fused for a long time with potassium nitrate, a small quantity of thallic oxide is formed, but the greater part of the chromate remains unaltered. If a mixture of thallium and potassium chromates is fused with the potassium nitrate, a crystallised double chromate, $KTlCrO_4$, is obtained. Lead chromate does not combine with thallium chromate.

When freshly prepared thallous chloride is treated with a highly concentrated solution of 20 parts of chromic acid, crystals of thallium chlorochromate, $TlCrO_3Cl$, separate. They are small prisms with a square base, and are decomposed by water with formation of thallous chloride and chromic acid. C. H. B.

Copper Hydrides. By A. LEDUC (*Compt. rend.*, **113**, 71—72).—On passing a stream of hydrogen for about two hours over a quantity of copper, contained in a combustion tube, heated to cherry-redness at the middle and to 300° at the ends, a solid of a hyacinth-red colour was formed at those parts which had reached, but not exceeded, dull redness, and when these parts were subsequently heated to bright redness in a stream of carbonic anhydride, the escaping gas was found to contain hydrogen, together with a little carbon monoxide. The substance is believed to be a new hydride of copper. JN. W.

Action of Water on Basic Copper Salts. By G. ROUSSEAU and G. TITE (*Compt. rend.*, **113**, 191—193).—Basic cupric nitrate, when heated with water in sealed tubes at 160° for 20 hours, is completely converted into black, amorphous cupric oxide, the water becoming strongly acid. The basic nitrate in the dry, solid state only decomposes at about 400°, and Rousseau has shown that it can be formed by heating concentrated solutions of cupric nitrate with marble between 180° and 330°.

Basic cupric sulphate is not decomposed by water below 220°, and decomposition is only complete after heating for 150 hours at 240—250°. As a rule, the cupric oxide is pseudomorphous after the basic sulphate, but sometimes it forms opaque, elongated prisms.

Atacamite is not affected by water at 200°; between 200° and 210° it darkens slightly, but at 240° the decomposition is almost complete after 24 hours. At this temperature, however, the oxychloride itself dissociates into the oxide and the chloride, so that the water plays no part except forming a solvent for the chloride.

Basic cupric phosphate is not affected by water at 275°, even after three days.

The decompositions are in accordance with thermochemical data, the reaction being determined at a moderately high temperature by the increase in the heat of solution of the liberated acid. The progress of the decompositions resembles the saponification of ethereal salts, as already observed by Saint Gilles in the case of ferric acetate.

C. H. B.

Copper Phosphates. By J. STEINSCHNEIDER (*Chem. Centr.*, 1891, ii, 51—52; *Dissertation, Halle*, 1890).—The author has obtained the following copper phosphates by the action of disodium hydrogen phosphate on copper sulphate:—

a. By employing an excess of copper sulphate, a double salt of the formula $3Cu_3P_2O_8,NaH_2PO_4$ is formed; if the copper sulphate be present in very large excess, Rammelsberg's normal phosphate, $Cu_3P_2O_8$, is formed. Both these salts, if subjected to protracted washing under pressure, are converted into the compound $4CuO,P_2O_5$, already described by Debray, Sarrazin, and Friedel. Sodium acetate precipitates the double salt $3Cu_3P_2O_8,NaC_2H_3O_2$ from the filtrate.

b. By employing an excess of sodium phosphate, two double salts are formed, namely, $2Cu_3P_2O_8,Na_2HPO_4$ and $3Cu_3P_2O_8,Na_2HPO_4$; the former is formed first and is converted into the latter by continued washing.

By the action of disodium hydrogen phosphate on cupric chloride, the following phosphates are formed:—

a. When an excess of cupric chloride is employed, the double salt $3Cu_3P_2O_8,2NaCl$ is principally formed, although sometimes it is mixed with the phosphate, $4CuO,P_2O_5$, and the oxychloride, $CuO,CuCl_2$; in one case the salt had the formula $5Cu_3P_2O_8,3NaCl$.

b. If an excess of the sodium phosphate is employed, the same phosphate, $3Cu_3P_2O_8,2NaCl$, is formed as in the case of employing an excess of cupric chloride.

By the action of the sodium phosphate on cupric nitrate, the following phosphates are obtained:—

a. By employing a slight excess of the cupric nitrate, the double salt $Cu_3P_2O_8,NaH_2PO_4$ is formed, whilst if the cupric nitrate is present in very large excess, the normal phosphate, $Cu_3P_2O_8$, together with a small quantity of basic cupric nitrate is obtained.

b. If the sodium phosphate is employed in excess, a double salt of the formula $18CuO,3Na_2O,8P_2O_5$, or $6Cu_3P_2O_8 + 3Na_2O,P_2O_5$, is formed, which is decomposed by washing.

The basic phosphate, $4CuO,P_2O_5$, with 1 mol. H_2O, is obtained by washing the normal phosphate, $Cu_3P_2O_8$, and corresponds with the mineral libethenite. If boiled with silver nitrate, it remains unchanged, whilst the normal cupric phosphate is quantitatively converted into cupric nitrate under similar conditions. With ammonia or ammonium carbonate, the basic phosphate dissolves very slowly, whilst cupric phosphate is readily dissolved by these reagents. Barium hydroxide decomposes the normal phosphate, but does not react with the basic phosphate. Potassium iodide reacts with the normal phosphate but not with the basic phosphate. Sodium thiosulphate dissolves the normal phosphate at ordinary temperatures, but the basic phosphate is only dissolved at a boiling heat.

If copper carbonate is warmed at 70° with phosphoric acid, the salt $3CuO,P_2O_5 + 3H_2O$ is obtained, whilst if the carbonate is neutralised with phosphoric acid, an acid salt, CuO,P_2O_5, is found in the filtrate. Whilst the phosphates of copper show, generally, a great similarity to the copper arsenates (this vol., p. 644), the phosphates corresponding with the arsenates $8CuO,3As_2O_5$ and $5CuO,2As_2O_5$ have not been prepared, and only the normal copper phosphate and double salts are obtained. On the other hand, whilst the normal phosphate is readily prepared by employing an excess of the reacting copper salt, the normal arsenate was obtained with difficulty.

J. W. L.

Erbium and Didymium. By G. Krüss (*Annalen*, **265**, 1—27). —It has been shown by Marignac, Soret, Nilson, Cleve, and Brauner that erbium earth, which, about 15 years ago, was considered to be the oxide of the element erbium, consists of at least seven different substances, namely, of scandium, ytterbium, thulium, erbium, terbium, the ytterite earth, and those earths denoted with X by Soret. The more recent researches of Lecoq de Boisbaudran have afforded evidence which proves that Soret's X-earth, or Cleve's holmium, consists of at least two elements, whilst Crookes' investigations have shown that the ytterite earth is composed of more than one oxide. The substance previously known as didymium has also been found to be a compound and to consist of samarium and the real didymium; according to Auer von Welsbach, the last-named substance consists of at least two "elements," neo- and praseo-didymium, both of which are probably compounds, as has been shown by Krüss and Nilson.

The author has made a number of experiments, with the object of isolating some of the constituents of the erbium and didymium groups, employing the best known methods; although it is possible in this way to obtain preparations in the spectra of which the relative intensities of the absorption lines are quite different from those usually observed, absolutely pure substances, whose molecular weights remain constant on further treatment, could not be obtained. Several new methods of separation have, therefore, been studied, and the older processes have also been subjected to a more rigorous examination; the results are given below.

The separation of the erbium and didymium earths can be partially effected by fractional crystallisation with potassium hydrogen sulphate; although in this way the didymium is accumulated in the first, and the erbium earths in the last, fractions, a complete isolation of the former was found to be impossible. Experiments were then made to try and separate the didymium by fractional precipitation with ammonia; for this purpose, a large quantity (rather more than 1 kilo.) of the mixed oxides obtained from gadolinite from Hitterö and Ytterby, was first freed from iron and some cerium, and then a neutral solution of the nitrates submitted to a systematic fractional precipitation with dilute ammonia. The spectrum of a concentrated solution of the nitrate of the didymium oxide obtained in this manner from the last fractions showed no erbium bands, and the nitric acid solution of the first fractions was quite free from didymium. The earths were, however, in both cases, mixed with colourless oxides, the didymium being probably accompanied by lanthanum, samarium, yttrium, and terbium, and the erbium by holmium, thulium, scandium, ytterbium, and cerium, assuming that all these substances were present in the original material. In order to prepare pure didymium oxide from the impure compound obtained as just described, it is first converted into the nitrate, the solution mixed with a large excess of soda, and then treated with chlorine, when the hydroxides of didymium, lanthanum, and of the colourless earths pass into solution, whilst the undissolved cerium hydroxide retains only a small quantity of didymium; the filtrate is then freed from chlorine, the earths precipitated with ammonia, and converted into nitrates. The almost neutral solution is now treated with potassium sulphate; the crystalline precipitate contains, besides didymium, some samarium and perhaps scandium and lanthanum, whilst yttrium and traces of samarium, erbium, terbium, and ytterbium, if present, pass into the filtrate; in the actual experiment, the filtrate seemed to contain principally yttrium and a small quantity of terbium. After repeating the treatment with potassium sulphate, the didymium potassium sulphate is precipitated with ammonia, the washed precipitate dissolved in sulphuric acid, and the anhydrous sulphate dissolved in ice-cold water; on gradually heating this solution, no separation of lanthanum sulphate occurred, so that the preparation evidently consisted of pure didymium sulphate. The atomic weight of the didymium present in this salt was found to be $R^{III} = 145$; its isolation from gadolinite in the manner described is a comparatively simple matter.

When a neutral solution of the chlorides of erbium, ytterbium, and yttrium in 50 per cent. alcohol is mixed with excess of a solution of aniline in the same solvent at 0°, no precipitation occurs; when, however, the mixture is kept for some time until it attains the ordinary temperature, a precipitate is gradually formed. In this way the various components of the solution can be partially separated from one another, as is shown by the fact that when a solution of a mixed oxide, $R^{III} = 161·81$, is subjected to this treatment, a precipitate, $R^{III} = 168·75$, and a filtrate containing an oxide, $R^{III} = 158·38$, are obtained.

When a neutral solution of the mixed gadolinite earths is treated with a concentrated solution of ammonium carbonate, kept for 24 hours, filtered, and the residue washed with ammonium carbonate, the precipitated basic didymium carbonate is almost free from erbium earths; on passing a stream of air through the filtrate, basic carbonates of the erbium earths, containing only a small quantity of didymium, are precipitated.

A partial separation of the didymium and ytterite earths can be effected by treating a solution of the mixed nitrates with a concentrated solution of potassium oxalate, digesting for 24 hours, and then filtering; the residue shows only slight indications of erbium lines on spectroscopic examination, and consists principally of didymium and holmium, whilst the filtrate is almost free from didymium, but contains considerable quantities of erbium and yttrium or scandium. When this filtrate is evaporated to dryness, ignited, and the residue extracted with water, a solution of scandium, containing only a little erbium, and probably also traces of didymium, is obtained.

By fractionally precipitating with alcohol, a neutral solution of the nitrate of the didymium ($R^{III} = 144—145$), obtained as described above, a nitrate of a colourless earth, which is insoluble in alcohol, is precipitated; atomic weight determinations made with a carefully purified sample of this earth gave $R^{III} = 111·6$ as the average of three experiments, and this value underwent no appreciable change on continuing the fractional precipitation with alcohol.

F. S. K.

Melting Point and Crystalline Form of Aluminium Chloride. By K. Seubert and W. Pollard (*Ber.*, **24**, 2575—2578).—The aluminium chloride was prepared by heating aluminium foil in a current of dry hydrogen chloride, and was quite white. The resublimed product melts at 193—194°, but sublimes and seems to boil at 175—179°. When heated in a closed tube at 200°, it is obtained, on cooling, in colourless, lustrous, six-sided tablets, which adhere to the walls of the tube. These crystals are mostly composed of three individuals twinned together, and show rhombic symmetry. The positions of extinction are 120° from one another. The apparent angle of the optic axis in air is about 12°. The crystals are optically negative.

E. C. R.

Action of Nitric Acid on Iron. By H. Gautier and G. Charpy (*Compt. rend.*, **112**, 1451—1453).—At the ordinary temperature, perfectly clean iron placed in nitric acid of specific gravity greater than 1·21 does not give any disengagement of gas; it is, however, slowly attacked, with formation of iron nitrate, traces of ammonia, and nitrogen peroxide, which remain in solution. The nitric acid which has been in contact with iron for some time gives a precipitate on neutralisation with potash. The following table shows the effect of acid of different concentrations on the weight of a piece of iron at the ordinary temperature:—

Acid of specific gravity		1·28	1·34	1·38	1·48	1·53
Percentage loss of weight for 24 hours during	(1) first two days	0·82	0·75	0·29	0·34	5·80
	(2) first ten days	0·59	0·45	0·25	0·33	5·75

The E.M.F. of an iron | platinum | nitric acid cell diminishes rapidly as the strength of the acid increases from a sp. gr. below 1·21 to higher densities. In the latter case, it is about 0·15 volt, and corresponds with solution of the iron, for, with circuits of different resistances, different intensities are obtained. By raising the temperature, the limit of specific gravity of the acid giving disengagement of gas and rapid attack is raised. At 60° it is only with concentrations above 1·38 that no disengagement of gas occurs. The limit is also raised by the presence of oxide on the surface of the iron; this is due to local heating caused by the solution of the oxide. If the iron be agitated in the acid until perfectly clean, it then behaves exactly as if the surface had not been coated with oxide. The same effect is produced if the oxide be electrolytically reduced.

The passive state of iron cannot be due to the production of a film of gas or of oxide upon the surface of the iron, but is probably produced by fuming nitric acid, owing to the modification which the latter causes in the oxide of iron, by which the oxide is rendered insoluble in the acid.

This modification probably consists in a dehydration, for if rusty iron be heated for some time at 140°, the acid of ordinary concentration no longer dissolves it with evolution of gas.

Nitric acid, whatever its concentration may be, attacks iron. The attack may be rapid and accompanied by evolution of gas, or, as is the case in the so-called passive state of iron, it may be slow and without disengagement of gas. W. T.

A Volatile Compound of Iron and Carbonic Oxide. Nickel-carbon-oxide. By BERTHELOT (*Compt. rend.*, **112**, 1343—1349).—Finely-divided iron is obtained by reducing carefully washed and dried, precipitated ferric oxide in hydrogen at the lowest possible temperature, or by heating ferrous oxalate and completing its reduction in hydrogen.

The reduced iron is treated with carbonic oxide at about 45°, when the gas becomes charged with a volatile iron compound. The charged gas is washed and burnt at the drawn-out extremity of a glass tube; the flame is whiter and brighter than that of carbonic oxide alone, and gives a characteristic spectrum. When a porcelain dish is held in the flame, a film is deposited, which dissolves in hydrochloric acid, yielding a solution which gives the ordinary iron reactions. The gas, when passed through a narrow glass tube heated to redness, deposits a metallic substance, consisting of iron with a little carbon. The charged gas, when treated with strong hydrochloric acid, yields iron chloride, and when confined in a flask partly filled with aërated water, a slow oxidation takes place, ferric oxide separating at the end of several days. The proportion of *iron-carb-*

onyl formed is very small, and the author did not succeed in isolating it (compare Mond and Quincke, Trans., 1891, **59**, 604).

Nickel-carbon-oxide (Mond, Langer, and Quincke, Trans., 1890, **57**, 749).—The liquid substance possesses a high vapour tension at ordinary temperatures; about a quarter of an atmosphere at 16°. It has no sensible dissociation tension at 16°, and a gaseous mixture of nitrogen and the vapour, containing 26 per cent. of the latter, has been kept over mercury for a month at about this temperature without any indication of change. The liquid may be kept unaltered under water, provided the vessel be completely filled with water free from air, and hermetically closed. The detonation observed by Mond, on rapidly heating the vapour, is not violent as compared with that of the nitro-compounds; the products of decomposition include a certain proportion of carbonic anhydride and carbon, as well as of carbonic oxide and nickel. It is this production of carbonic anhydride which determines the decomposition; a simple resolution of the nickel-carbon-oxide into nickel and carbonic oxide would be inexplicable in view of the formation of this substance at 30° by direct synthesis. The decomposition of carbonic oxide into carbonic anhydride and amorphous carbon gives for 12 grams of carbon +38·8 cal. If the heat of formation of $Ni(CO)_4$ be less than 77·6 cal. by the direct union of nickel and carbonic oxide, explosion could occur by intramolecular combustion; according to the author, if exploded by the shock of an energetic detonator, such as mercury fulminate, the decomposition would occur solely in accordance with the equation $NiC_4O_4 = Ni + 2CO_2 + 2C$. With a slower reaction, effected at a lower temperature, more or less nickel-carbon-oxide may be simultaneously decomposed into nickel and carbonic oxide, the heat required being supplied by the portion undergoing intramolecular combustion.

A mixture of the vapour with oxygen or air burns or explodes on contact with a very hot substance, according to the relative proportions of the vapour and oxygen present. The explosion of a mixture of dry nickel-carbon-oxide with oxygen may be brought about by simple energetic agitation over mercury. The same gaseous mixture in presence of a little water oxidises slowly, with formation of a greenish, gelatinous precipitate. This compound contains nickel, oxygen, water, and some combined carbon; it blackens from separation of carbon on heating. Simultaneously with the production of this complex oxide in the cold, carbonic oxide is regenerated. The dry mixture undergoes a similar decomposition, but the oxide formed is yellowish-brown; in time it blackens by further decomposition.

Liquid nickel-carbon-oxide kept under water without exclusion of air decomposes in a similar manner, but more slowly. Nickel-carbon-oxide thus behaves in a manner analogous to the organo-metallic radicles and the metallic derivatives of acetylene.

In contact with concentrated sulphuric acid, dry nickel-carbon-oxide detonates after a few moments. A mixture of the vapour with nitrogen reacts quietly with the same acid, producing nickel sulphate and 4 vols. of carbonic oxide, the acid undergoing reduction. Concentrated potash seems to have no action. Pure ammonia gas does not act on nickel-carbon-oxide, at least immediately, but if oxygen be gradually added to the mixture, a whitish complex substance, blackening when heated, is deposited.

Hydrogen sulphide rapidly precipitates a black sulphide from the vapour in the cold; hydrogen phosphide similarly causes the deposition of a black, shining compound.

Nitric oxide, passed into liquid nickel-carbon-oxide, or mixed with its vapour volatilised in nitrogen, produces blue fumes, slowly deposited. The addition of a further quantity of nitric oxide, even when its initial volume was four times that of the gaseous nickel-carbon-oxide, reproduces these fumes. The inference is drawn that the vapour of another nickel compound is present as well as the nickel-carbon-oxide, and forms a blue compound immediately with nitric oxide, which is present in excess. If a few bubbles of oxygen be introduced in place of the second quantity of nitric oxide, a blue compound, different from the one noticed above, is formed.

The author calls attention to the part probably played by the compound of iron and carbonic oxide in metallurgical processes, such as Siemens' and the cementation processes, and to the possible explanation afforded of the precipitation of carbon from carbonic oxide by iron, observed by Gruner, and of Cailletet's observations of the formation of gaseous bubbles in the interior of softened iron.

W. T.

Volatilisation of Nickel and Iron in presence of Carbonic Oxide. By J. GARNIER (*Compt. rend.*, **113**, 189—191).—Some time ago the author observed the luminosity of the flame of carbonic oxide formed in the manufacture of iron and steel, and the separation of nickel and nickel oxide in the flues of a furnace in which ferronickel was heated. He considers that these phenomena were due to the formation of the volatile compounds of iron and nickel with carbonic oxide.

C. H. B.

Volatility of Nickel in presence of Hydrogen Chloride. By P. SCHÜTZENBERGER (*Compt. rend.*, **113**, 177—179).—When dry hydrogen is passed over anhydrous nickel chloride heated to dull redness, and the tube through which the gas escapes is heated to dull redness at any point, a white deposit of nickel chloride takes place at that point. The volatile substance is not removed by passage of the gas through glass wool and along a considerable length of tube at the ordinary temperature. Similar results are obtained when hydrogen chloride is passed over finely-divided nickel, and it is evident that a gaseous compound containing nickel is formed. This gas has most probably the composition $NiClH$, and reacts with hydrogen chloride when heated, in accordance with the equation $NiHCl + HCl = NiCl_2 + H_2$.

C. H. B.

Cobalt Dioxide. By G. VORTMANN (*Ber.*, **24**, 2744—2749).—Pure cobalt sulphate is dissolved in water and treated with decinormal iodine solution and pure soda, at a temperature of 50—60°, the liquid is filtered, the filtrate acidified, and the excess of iodine determined in the usual manner. As the result of 25 experiments, the composition of the precipitate is found to vary from $Co_{10}O_{16\cdot65}$ to $Co_{10}O_{19\cdot27}$. It doubtless consists chiefly of *cobalt dioxide*, which is, however, very unstable. Its formation appears to be dependent on a variety of conditions. Cobalt dioxide has a greenish-black colour, and decomposes at 100°. The oxidation of the cobalt is not facilitated by the employment of a more concentrated iodine solution, or by the presence of aluminium, iron, zinc, or magnesium salts. It appears probable that the compound formed by the action of argentic oxide on cobaltous oxide is not represented by the formula Ag_4O,Co_2O_3, as stated by H. Rose, but that it is a mixture of finely divided silver and cobalt dioxide, or the corresponding hydroxide.

J. B. T.

Action of Heat on Solutions of Chromic Salts. Green Salts of Chromium. By A. Recoura (*Compt. rend.*, **112**, 1439—1442).—The author proves, by thermochemical methods, that the green solutions obtained by heating solutions of the normal violet chromic salts contain free acid and a soluble basic salt, and further, that such solutions contain a particular variety of chromic oxide.

A solution of a chromic salt, such as the sulphate or chloride, when heated on a water-bath at 100°, emits acid vapours, whereas the solid salt at the same temperature is not decomposed. The amount of free acid present in the green solution of the sulphate was determined by adding a definite quantity of soda solution, and measuring the heat disengaged; so long as this equalled the heat of neutralisation of free sulphuric acid, there was at least the amount of free acid present equivalent to the soda used. A control to the final result was obtained by adding an equivalent amount of sulphuric acid after the addition of the soda; if no excess of soda were added in the first place, there was merely a slight absorption of heat, due to the action of the acid on the sodium sulphate previously formed.

A large number of experiments, conducted at different degrees of dilution, gave the formula of the soluble basic sulphate as $2Cr_2O_3,5SO_3$. This salt contains a modified oxide, which cannot exist in the free state; the oxide precipitated from the green solution by alkalis forms, on redissolving, a new basic salt, $Cr_2O_3,2SO_3$.

W. T.

New Process for the Manufacture of Chromates. By J. Massignon and E. Vatel (*Bull. Soc. Chim.* [3], **5**, 371—376).—The author describes the following process, which is based on the fact that when chromium oxide is heated with a mixture of calcium chloride and oxide, a chromite is formed, which absorbs oxygen from the air to yield a calcium chromate. The finely powdered mineral is mixed with a paste composed of lime, calcium carbonate, and a concentrated solution of calcium chloride in such proportion that the lime and calcium carbonate are slightly in excess of the amount necessary to combine with the chromium oxide present, whilst the calcium chloride is about one-third of the total lime used. The mixture, on exposure to air, hardens, and is moulded into bricks, which are dried and subsequently roasted at a temperature sufficient to convert the calcium carbonate into lime. The bricks are exposed to the action of the air for about a month, then lixiviated with hot water to remove the calcium chloride, and the residue containing the calcium chromate is treated with alkali carbonate or sulphuric acid in the usual way, according as an alkali chromate or chromic acid is required. T. G. N.

Reaction of Chromic Acid with Barium Hydroxide in presence of Oxygen. By E. PÉCHARD (*Compt. rend.*, **113**, 39—41).—When a dilute aqueous solution of chromic acid (8 grams per litre) is treated at a low temperature with excess of oxygen dissolved in water, and barium hydroxide is added in slight excess, a precipitate, at first yellowish, but afterwards darker, is thrown down, and oxygen begins to be evolved; if the whole is then poured rapidly into a large excess of water, the precipitate may be collected and dried in a vacuum over sulphuric acid.

The substance thus obtained explodes with a sharp report when heated in a test-tube, leaving a residue which appears to consist of barium chromate mixed with a little barium oxide. With dilute sulphuric acid, it gives a fine blue colour, which, however, soon disappears, with evolution of oxygen. Its composition is represented approximately by the formula $BaCrO_5$. JN. W.

Zirconates of the Alkalis. By L. OUVRARD (*Compt. rend.*, **112**, 1444—1446).—Zirconium oxide, when fused with lithium carbonate, rapidly decomposes it with liberation of carbonic anhydride; after six or eight hours fusion over a Bunsen flame, a mass is obtained which, on treatment with boiling water slightly acidified with acetic acid, yields a crystalline powder consisting of zirconium oxide free from lithium. Finely pulverised zircon yields the same result. On substituting lithium chloride for the carbonate, and cooling the fused mass slowly, flat prisms, with longitudinal extinction, often corroded, are obtained on treating it with water. These crystals are readily attacked by acids, and consist of Li_2ZrO_3.

Crystallised zirconium oxide only is obtained by fusion of the oxide with potassium carbonate. Finely-powdered zircon heated with potassium carbonate to bright redness for 15 minutes yields well developed, tabular crystals of the silicozirconate K_2SiZrO_5. These are prisms having longitudinal extinction, and are attacked by hydrofluoric acid and by ammonium hydrogen sulphate. If the reaction is prolonged for an hour and a-half at the same temperature, crystallised zirconium oxide alone is obtained. Here zircon silicate behaves like a true acid. A further example will be given among the alkaline earthy combinations to be described. Sodium carbonate yields no compounds. W. T.

Zirconates of the Alkaline Earths. By L. OUVRARD (*Compt. rend.*, **113**, 80—82).—When zirconium oxide is fused with calcium chloride at a red heat for 20 or 30 hours, it becomes crystalline; and on extracting the melt with water, optically active, striated crystals of calcium zirconate, $CaZrO_3$, insoluble in acids, and isomorphous with calcium stannate and titanate (peroffskite), are left behind.

Strontium and barium zirconates are prepared in a similar manner.

If finely-powdered zircon is substituted for the oxide, and the temperature is raised to a white heat, clean rhombic crystals of calcium silicozirconate, $CaSiZrO_5$, are obtained, isomorphous with artificial sphene and calcium silicostannate. Jn. W.

Antimony Pentasulphide. By T. Wilm (*Zeit. anal. Chem.*, **30**, 428—446).—Preparations passing under the name of "Golden Sulphide of Antimony (Goldschwefel)," and having a composition agreeing with the formula Sb_2S_5, but from different makers, give very varying results when used in the vulcanisation of caoutchouc. In the course of a study of two such samples, the author has prepared the so-called antimony pentasulphide of the text-books by the following methods:—(1) By mixing a solution of sodium thioantimonate (Schlippe's salt) with a slight excess of dilute sulphuric acid; (2) by precipitating with hydrogen sulphide a clear solution of potassium antimonate under various conditions, (*a*) alone, (*b*) after addition of tartaric acid, (*c*) of both tartaric acid and a small quantity of hydrochloric acid, (*d*) of tartaric acid and a large quantity of hydrochloric acid; in case *c* the precipitation was performed in two fractions; (3) by passing hydrogen sulphide through an aqueous solution of commercial antimony trichloride, which had first been saturated with chlorine, then warmed on the water-bath until the odour of chlorine had disappeared, and mixed with tartaric acid; (4) by the action of hydrogen sulphide on a solution (mixed with tartaric acid) of commercial antimony pentachloride. Preparation 1 when dry formed dense, hard, brittle, dark-brown grains; those thrown down by hydrogen sulphide were loose, bulky, soft, orange-yellow masses. The composition of these preparations and their behaviour when treated with carbon bisulphide are shown in the following table. Preparation 1 had been dried in the desiccator; the others by heat:—

	Preparation.								Commercial products.	
	1.	2*a*.	2*b*.	2*c*, 1st fraction.	2*c*, 2nd fraction.	2*d*.	3.	4.	A.	B.
Total sulphur....	40·7	38·1	39·0	39·8	37·1	39·4	41·3	38·6	41·9	40·4
Sulphur extracted by CS_2........	7·9	13·9	11·7	12·2	8·2	8·4	6·4	13·8	13·3	8·9
Difference.......	32·8	24·2	27·3	27·6	28·9	31·0	34·4	24·8	28·6	31·5

Since Sb_2S_5 contains 39·58 and Sb_2S_3 28·23 per cent. of sulphur, it will be seen that the composition of the original preparation varied somewhat considerably from that of the pentasulphide, whilst that of the residue varied still more widely, the sulphur extracted being in three cases more than would agree with the original existence of a mixture of the composition $Sb_2S_3 + S_2$. Preparation A invariably gave good results in vulcanising; B, on the contrary, bad results; the technical method of judging of the value of a preparation from an estimation of the sulphur which it gives up to carbon bisulphide seems therefore by no means trustworthy.

A property of the pentasulphide hitherto unnoticed is its volatility and oxidation even at 100°. Preparation 1, which, after drying in the desiccator, gave up no antimony to tartaric acid, lost weight considerably during 15 hours at 120°, continued thereafter to lose at 100—110°, and subsequently gave up antimony to tartaric acid.

To ascertain the influence which the above facts would have on Bunsen's method of separating arsenic and antimony by precipitating the latter as pentasulphide from the oxidised solution, washing with water, alcohol, carbon bisulphide, and again alcohol, drying at 110°, and weighing as pentasulphide, a preparation was made according to Bunsen's instructions, with the exception that tartaric acid was added to dissolve a white precipitate which separated whilst passing chlorine. During the washing with water, much of it assumed a colloïdal form, and refused to subside. After washing with water and alcohol only, it was divided into two portions, one of which was without drying treated with carbon bisulphide. It gave up a considerable quantity of pure sulphur. After drying over sulphuric acid in the cold, it contained 39·96 per cent. of sulphur, of which 3·59 per cent. was soluble in carbon bisulphide. Preparations by method 1 likewise gave up sulphur to carbon bisulphide before drying. It appears, therefore, that accurate results cannot be obtained by Bunsen's process. M. J. S.

Action of Phosphorus Pentafluoride on Heated Spongy Platinum. By H. MOISSAN (*Bull. Soc. Chim.* [3], **5**, 454—456; compare Abstr., 1886, 592).—When phosphorus pentafluoride acts on pure platinum sponge at a temperature slightly above dull redness, a volatile, crystalline compound condenses in the cooler portion of the tube; this has the formula PF_3,PtF_2, analogous to the compound $PCl_3,PtCl_2$ discovered by Schützenberger. T. G. N.

Osmium: Osmiamic Acid and Osmiamates. By A. JOLY (*Compt. rend.*, **112**, 1442—1444).—*Preparation of Potassium Osmiamate.*—100 parts of osmium tetroxide is dissolved in 100 parts of potash with 50 parts of water; the solution is kept at about 40° and 40 c.c. of ammonia solution added. In a short time, the brown liquid is decolorised, and a clear, yellow, crystalline precipitate of potassium osmiamate is deposited; it recrystallises from its solution in boiling water in fine, quadratic octahedra.

The reaction is not accompanied by any escape of gas. Taking the atomic weight of osmium as 190, the formula $KNOsO_3$ agrees better with the results obtained by Fritzsche and Struve (*Bull. Acad. St. Pétersbourg*, **6**, 81) than that proposed by them, $K_2N_2Os_2O_5$; this is supported by the author's determinations of potassium and nitrogen, and by the non-formation of a gas, $OsO_4 + KOH + NH_3 = KNOsO_3 + 2H_2O$.

Heated in a vacuum above 200°, potassium osmiamate is rapidly decomposed with evolution of nitrogen. At 440°, nearly the whole of the nitrogen is eliminated. The solid products of the decomposition differ according to the temperature employed; at 350°, potassium osmite and osmium dioxide remain; at 440°, an indigo-blue, crystalline substance is formed; it is insoluble in water, and is scarcely attacked by concentrated hydrochloric acid; its composition is represented by the formula $KOsO_3$. This salt would correspond with an acid $HOsO_3$ and an oxide Os_2O_5; the study of these compounds will be followed up in view of the known existence of a ruthenium oxide Ru_2O_5. Osmiamic acid, $OsNO_2 \cdot OH$, may be viewed as a first anhydride of $OsNO(OH)_3$, the hypothetical analogue of the nitroso-compounds of ruthenium, $RuNOCl_3$ and $RuNO(OH)_3$, previously described. W. T.

Mineralogical Chemistry.

Native Iron of Terrestrial Origin from Berezowsk. By Daubrée and S. Meunier (*Compt. rend.*, **113**, 172—177).—Two specimens, weighing respectively 11·5 and 72·0 grams, were found in the auriferous deposits at Berezowsk, in the Ural, near Ekaterinbourg. They have evidently been subjected to great pressure and a contorting shearing stress. The metal is very magnetic, but shows no polarity; sp. gr. at 17° = 7·59. A cut and polished surface has the appearance of iron, and when treated with acid is attacked uniformly. It dissolves completely in concentrated hydrochloric acid; nickel is absent, but platinum is present in small quantity, seemingly about 0·1 per cent. Platiniferous iron obtained by the simultaneous reduction of ferrous chloride and platinic chloride in a current of hydrogen is likewise completely soluble in hydrochloric acid.

The minerals associated with the native iron are quartz, mica, peridote, pyroxene, serpentine, triclinic felspars, magnetite, and chromite. The platiniferous iron of Nichne-Tagilsk is also associated with peridotic rocks and with chromite, and the same is true of the nickeliferous iron from New Zealand and Piémont.

The compact character of this native iron indicates that it has not been reduced from the oxide by the action of reducing gases, and it seems most probable that it comes from infra-granitic depths where there is a deficiency of oxygen. C. H. B.

Formation of Natural Sulphides. By E. Chuard (*Compt. rend.*, **113**, 194—196).—Bronze implements found in lake mud containing organic matter are often covered with a thin layer of a pale-yellow colour, and with a metallic lustre. This layer is easily detached and is friable, yielding a greenish powder without metallic lustre. One specimen had the following composition: S, 27·09; Sn, 5·07; Fe, 31·05; Cu, 33·97; the remainder consisting of zinc and organic matter. It, therefore, agrees very closely with stanniferous copper pyrites, and is an example of a sulphide formed without the intervention of any mineral water. (Compare Daubrée, *Compt. rend.*, **80**, 461.)

C. H. B.

Iron Pyrites containing Nickel and Cobalt. By E. W. Neubert and F. Kollbeck (*Jahrb. f. Min.*, 1891, ii, Ref. 292—293; from *Jahrb. Berg. Hütt. Sachsen*, 1889, 106).—In the Himmelsfürst mine, at Freiberg, in Saxony, iron pyrites occurs in copper pyrites in the form of reddish-yellow grains, having a sp. gr. of 4·85 to 4·95. Analysis gave results in accordance with the formula $48FeS_2 + 7NiS_2 + 4CoS_2$.

B. H. B.

Eukairite, Umangite, and Luzonite from the Argentine. By F. Klockmann (*Zeit. Kryst. Min.*, **19**, 265—275).—In a collection of Argentine minerals presented to the School of Mines at Clausthal, the author has found three rare minerals of great interest.

1. *Eukairite.*—This rare mineral, which in Europe is known only at one Swedish locality, gave on analysis results in accord with the formula AgCuSe. The mineral occurs in the province of La Rioja in veins in limestone.

2. *Umangite.*—Associated with eukairite, there occurs a mineral, thought to be peacock-copper ore, which proved on analysis to be a variety of copper selenide. The analytical results obtained were as follows:—

Cu.	Ag.	Se.
56·03	0·49	41·44

The formula, therefore, is Cu_3Se_2. Among all the known minerals there is no analogous compound of copper and selenium. The new mineral occurs in finely granular masses, with a hardness of 3·0 and a sp. gr. of 5·62. The lustre is metallic, and the colour cherry-red to violet.

3. *Luzonite.*—This mineral was discovered in 1874 by A. Weisbach. It exhibits the external characters of famatinite, and the chemical composition of enargite. Specimens of luzonite from a new locality, the Sierra de Famatina, gave on analysis results according well with those obtained by Winkler when analysing luzonite from Mancayan.

B. H. B.

Plumboferrite, a New Swedish Mineral. By L. J. Igelström (*Zeit. Kryst. Min.*, **19**, 167—170).—This mineral approaches most closely to franklinite and to Damour's jacobsite. In plumboferrite, however, the base is lead oxide instead of zinc oxide, as in franklinite, or manganous oxide, as in jacobsite. Plumboferrite occurs in the Jakobsberg manganese mine at Nordmarken, in veins in the granular limestone. On analysis, the mineral gave results corresponding with the formula $2Fe_3O_4 + PbFe_2O_4$.

B. H. B.

Mineralogical Notes. Antlerite. By W. F. Hillebrand (*Jahrb. f. Min.*, 1891, ii, Ref. 38—40; from *Bull. U.S. Geol. Surv.*, **55**, 48—55).

—The bulletin contains a number of interesting analyses of minerals. Analyses are given of samarskite, of a zircon mineral, probably a mixture of cyrtolite, limonite, and a phosphate, and of white beryl.

A bright green mineral from the Antler mine, Arizona, gave on analysis—

CuO.	ZnO.	CaO.	SO_3.	H_2O.	Sp. gr.
68·19	0·29	0·05	20·46	11·11	3·93

This composition corresponds with the formula $3CuSO_4 + 7Cu(OH)_2$. The author suggests for this mineral the name of *antlerite*, if on further investigation it should prove to be a new species.

B. H. B.

Barytes from Rumelange. By G. Cesàro (*Jahrb. f. Min.*, 1891, ii, Ref. 7—8; from *Bull. Soc. géol. Belg.*, **14**, 10).—In a large ammonite from the oölitic iron ore of Luxemburg, crystals of barytes occur between crystals of calcite. The barytes crystals exhibit the following forms: $0P$, ∞P, $\infty\bar{P}\infty$, $\infty\bar{P}2$, $\infty\breve{P}\infty$, $\infty\breve{P}3$, $\frac{1}{2}\bar{P}\infty$, $\frac{1}{4}\bar{P}\infty$, $\frac{1}{6}\bar{P}\infty$, $\breve{P}\infty$, P, $\frac{1}{6}P$. The face $\frac{1}{6}\bar{P}\infty$ has not hitherto been observed.

B. H. B.

Minerals from Tarapaca. By H. Schulze (*Jahrb. f. Min.*, 1891, ii, Ref. 21—22; from *Verh. deutsch. wissen. Vereins zu Santiago*, **2**, 49—60).—In the alum deposits of the province of Tarapaca, the author has found soda alum in large quantities, pickeringite in fibrous masses, and bloedite and tamarugite, two minerals hitherto unknown in the district. On analysis, the minerals gave the following results:—

	SO_3.	Al_2O_3.	MgO.	CaO.	CuO.	CoO.	Cl.	Na_2O.	H_2O.	Total.
I.	48·07	—	12·12	—	—	trace	—	18·39	21·60	100·18
II.	45·66	14·48	—	0·20	trace	—	0·12	9·04	30·86	100·36
III.	37·28	11·85	4·64	0·31	0·01	0·01	0·02	—	46·10	100·22

I. Bloedite; formula $Na_2SO_4,MgSO_4 + 4H_2O$. II. Tamarugite; formula $Na_2SO_4,Al_2S_3O_{12} + 12H_2O$. For this new mineral the author suggests the name of tamarugite, from the Pampa del Tamaruga. III. Pickeringite; formula $MgSO_4,Al_2S_3O_{12} + 22H_2O$. B. H. B.

Place of Långbanite in the Mineral System. By H. Bäckström (*Zeit. Kryst. Min.*, **19**, 276—283).—Four years ago G. Flink described a new mineral, which he termed lånbganite. The mineral occurred in hexagonal crystals, and had the curious composition represented by the formula $37Mn_5SiO_3 + 10Fe_3Sb_2O_8$. It is not easily seen what place in the mineral system should be assigned to a mineral of so peculiar and complicated a composition. In order to throw further light on the question, the author has subjected this mineral to a fresh examination, with the following results:—

	Sb_2O_5.	SiO_2.	MnO.	FeO.	CaO.	MgO.	Total.
I.	13·96	9·58	65·44	3·10	1·73	0·53	94·34
II.	17·03	8·75	60·72	4·27	2·98	0·40	94·15
III.	15·41	10 88	66·29	10·32	—	—	102·90

For these analyses there were employed for I 0·7704 gram, and for II 0·7746 gram, the results being calculated so as to correspond with the analysis published by Flink (III). Correcting these analyses, under the assumption that manganese is present as Mn_2O_3 and MnO and antimony as Sb_2O_3, the totals of the author's analyses amount to nearly 100 per cent. Långbanite may, therefore, be considered to be a mixture of compounds having the general formula $R_mR_nO_3$, in which $m + n = 6$. It is, however, not isomorphous with iron glance and titaniferous iron, but has an axial ratio of 1 : 0·8219, corresponding with that of the calcite series. B. H. B.

Artificial Datholite. By A. De Gramont (*Compt. rend.*, **113**, 83—84).—A mixture of 25 grams of powdered borax and 5 grams of precipitated calcium silicate was heated in a platinum-lined steel pressure-tube at 400° for 36 hours. Besides other products, the melt yielded 1·5 grams of a crystalline powder, which had the composition and presented all the characters of natural datholite:—

	SiO_2.	CaO.	H_2O.	FeO.	B_2O_3.	Density.
Artificial I ...	35·39	35·95	6·65	1·19	20·82	3·05
Artificial II ...	—	35·96	6·37	—	—	—
Datholite from Andreasberg ..	37·36	35·67	5·71	—	21·26	2·9
Botryolite from Arendal	36·0	39·5	6·5	1·0	17·0	2·85

The iron was due to the impurity of the calcium silicate.

Jn. W.

Rhyolites from Sweden. By N. O. Holst (*Jahrb. f. Min.*, 1891, ii, Ref. 86—87).—On the Island of Ramsö, in the Lake of Mien, Sweden, a peculiar rock of volcanic character occurs, and this the author describes as rhyolite. Although the rock occurs in so limited an area, there are several distinct types. Descriptions and analyses of seven of these are given by the author. In the pumice-like variety, crystals of A. Schmidt's beaumontite are met with. An analysis of this mineral gave the following results:—

SiO_2.	Al_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
59·83	16·40	1·05	5·28	1·78	1·08	14·78	100·20

B. H. B.

Oligoclase and Biotite from Gailbach. By E. Goller (*Jahrb. f. Min.*, Beilage **6**, 485).—The author gives analyses of oligoclase (I) and of biotite (II) from the diorite-gneiss of Gailbach. The results were as follows:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	66·89	0·11	17·95	0·72	—	3·60	1·18	4·68	4·14	0·33	99·60
II.	37·98	1·82	18·20	1·19	12·16	3·45	13·93	5·95	1·44	2·61	98·73

The oligoclase thus has the composition Ab_2An_1; its sp. gr. is 2·665; that of the biotite is 3·072. B. H. B.

Wernerite from Chili. By E. JANNETTAZ (*Jahrb. f. Min.*, 1891, ii, Ref. 28; from *Bull. soc. fran. de min.*, **12**, 445—446).—Some specimens exhibited in Paris as tourmaline, consisting of long, fibrous prisms from the Llanca mine, Coquimbo, proved on examination to be dipyre (wernerite). Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	Ignition.	Total.
57·4	19·6	3·4	6·2	0·4	8·8	3·41	99·21

B. H. B.

Sigterite and Albite from Sigterö. By C. A. TENNE (*Jahrb. f. Min.*, 1891, ii, Mem. 206—210).—A year ago Rammelsberg published a note on a new variety of felspar, sigterite, from Sigterö, near Brevig. The interpretation of the analysis was based on the results of an optical examination which proved that the felspar resembled albite crystallographically, whilst the chemical analysis indicated a much more basic member of the felspar series. An examination of a second felspar, albite, occurring in association with sigterite, shows that the angles measured on the two minerals are identical. Further examination of the sigterite proves that it is a mixture of elæolite and albite, a conclusion with which Rammelsberg concurs.

B. H. B.

Natrolite of Montecatini. By E. MATTIROLO (*Zeit. Kryst. Min.*, **19**, 203; from *Atti Accad. Sci. Torino*, **21**).—The mineral discovered by Meneghini, in 1852, in the serpentine rocks of Tuscany was thought to be a new species differing from natrolite, inasmuch as it contained magnesia, and was therefore named *savite.* Sella pointed that out the mineral was crystallographically identical with natrolite. A careful analysis made by the author shows that magnesia and iron are entirely absent, and that the identity of savite and natrolite is unquestionable. B. H. B.

Natrolite. By G. B. NEGRI (*Jahrb. f. Min.*, 1891, ii, Ref. 230; from *Rivista min. crist. ital.*, **7**, 16—20).—Natrolite from the collection of the University of Padua, carefully selected and purified, gave on analysis the following results:—

	SiO_2.	Al_2O_3.	Na_2O.	K_2O.	H_2O.	Total.
I.	47·21	27·01	15·99	—	9·55	99·76
II.	46·97	27·12	15·95	0·40	9·42	99·86
III.	47·23	27·21	14·80	0·41	9·70	99·35
IV.	47·71	27·89	16·99	—	9·69	102·28

The mineral was derived from the following localities:—I, Salcedo; II, Montecchio Maggiore; III, Lugo; IV, Alta Villa. The analytical results are in accord with the formula $Na_2Al_2Si_3O_{10} + 2H_2O$. B. H. B.

Amorphous Minerals from Budapest. By F. KOCH (*Zeit. Kryst. Min.*, **19**, 198—199; from *Vegytani lapok*, **5**, 9—11).—The author gives analyses of two minerals obtained from the place, near Budapest, where the dolomite is in contact with the overlying marl.

At this contact the marl is converted into a reddish-brown, porous substance, on which a yellowish mineral (I) and a chalk-like, white substance (II) occur:—

	SiO_2.	Al_2O_3.	CaO.	MgO.	Fe_2O_3.	Ignition.	Total.
I.	40·48	30·06	2·92	0·33	trace	25·53	99·32
II.	18·41	43·35	1·23	trace	trace	36·64	99·63

The yellow mineral is thought by the author to be halloysite.

B. H. B.

Chloritoïd from Champion, Michigan. By H. F. KELLER and A. C. LANE (*Zeit. Kryst. Min.*, **19**, 383—385).—Since 1880, chloritoïd has been known to occur in the upper peninsula of Michigan. The authors have, however, discovered it further west, at the Champion mine, in the form of dark-green, curved plates attaining a diameter of several centimetres, with a thickness in places of 4 mm. Its hardness is 6·5, and its sp. gr. 3·552. Analysis yielded the following results:—

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
24·29	0·28	34·00	10·55	20·52	1·29	0·59	0·97	0·35	6·75	99·59

The formula deduced from these analytical results is

$$Si_8O_{55}(Al,Fe)_{16}(Fe,Mg)_7(H,K,Na)_6,$$

which differs from that of sismondine merely in the larger proportion of water present. The mineral occurs in an altered greywacke.

B. H. B.

Artificial Hornblende. By K. v. CHROUSTCHOFF (*Jahrb. f. Min.*, 1891, ii, Mem. 86—90).—Hornblende has not hitherto been prepared artificially. The author has, however, obtained successful results by employing a pear-shaped vessel of very thick glass, with a capacity of 25 c.c. A special furnace was erected for the reception of 12 of these vessels. They were filled with (1) a solution of colloïd silica containing 3 per cent. of silica, (2) an aqueous solution of alumina, (3) an aqueous solution of ferric hydroxide, (4) ferrous hydroxide, (5) lime water, (6) freshly prepared magnesium hydroxide suspended in water, and (7) a few drops of soda potash solution. Vessels filled with these ingredients were heated in the furnace for three months at 550°. At the end of the experiment, it was found that the interior of the vessel consisted of a greenish-brown mass containing hard grains, which, when washed out, proved to be distinct, dark, prismatic crystals exhibiting the crystallographical characters and possessing the chemical composition of hornblende. Besides hornblende, the other crystallised products formed were (1) pyroxene resembling diopside, (2) colourless, regular crystals, probably analcime, (3) very fine quartz crystals up to 2 mm. in length, and (4) thin tablets of orthoclase.

B. H. B.

The Basalt of the Stempel, near Marburg. By M. BAUER (*Jahrb. f. Min.*, 1891, ii, Mem. 156—205).—This is the first instalment of an elaborate monograph on the basalt occurring at the hill known as the Stempel which rises above the sandstone of the Lahn plateau. The rock is best known on account of the zeolites, notably philippsite, which it contains. An analysis of the unaltered normal rock gave the following results:—

SiO_2.	TiO_2.	P_2O_5.	FeO.	Al_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
46·14	1·07	1·46	10·56	13·10	12·55	9·97	2·02	2·61	1·02	100·50

Of this rock and of the interesting minerals it contains, the author gives a detailed description based on microscopic observations.

B. H. B.

Basaltic Rocks of Hessen. By H. WOLFF (*Jahrb. f. Min.*, 1891, ii, Ref. 278—280; from *Sitzungsber. phys. med. Soc. Erlangen*, **22**, 118—140).—In connection with the geological survey of Niederaula and Neukirchen by the officers of the Prussian Government, the author has made a careful chemical examination of the basaltic rocks which have been collected during the progress of the work. He gives four analyses of felspar-basalts, seven analyses of basanites, and two analyses of nepheline-basalt. In appearance these rocks differ but slightly, the differences being solely in chemical composition.

B. H. B.

Rocks and Minerals from Corsica. By G. RUPPRECHT (*Jahrb. f. Min.*, 1891, ii, Ref. 289—291).—The author gives analyses of (1) granite from Ajaccio, (2) grey quartz-porphyry from Ajaccio, (3) finely-granular, red muscovite-granite from Apielto, (4) large, pink felspars (orthoclase) from the granitite of Solario, of Apielto, and of the Couvent de la Trinité, (5) albite from the same rocks, (6) black mica from the Couvent de la Trinité rock, (7) hornblende, and (8) felspar from the diorite from the Valle d'Orezza.

B. H. B.

Chalybeate Waters containing Free Sulphuric Acid. By E. WILLM (*Compt. rend.*, **113**, 87—89).—The mineral waters of Rennes-les-Bains (Aude), which contain ferrous, aluminium, calcium, magnesium, and sodium sulphates, and sodium chloride, have a powerfully acid reaction, due to the presence of from 1·17 to 17·01 parts per 100,000 of free sulphuric acid. Surface efflorescences, consisting of ferric and aluminium sulphates with siliceous matter, have been observed in an old jet quarry in the neighbourhood of the well yielding the largest proportion of acid. JN. W.

Organic Chemistry.

Mechanical Determination of the Arrangement of the Carbon Atoms in Organic Compounds. By G. HINRICHS (*Compt. rend.*, **113**, 313—315).—In the structural formulæ for the normal paraffins, the carbon atoms are shown as forming a straight line. All those properties which depend solely on structure should be continuous functions of the number of carbon atoms in the molecule, whether the number of carbon atoms is even or uneven. The melting points of the paraffinoïd hydrocarbons containing an uneven number of carbon atoms are less, however, than they should be according to the above rule. If the melting point is a function of the moment of inertia of the molecule for its natural axis of rotation, the author shows that the above fact would lead to the arrangement of the carbon atoms in a zig-zag line. H. C.

Action of Boron Fluoride on Nitriles. By G. PATEIN (*Compt. rend.*, **113**, 85—87).—Boron fluoride combines in molecular proportions with aliphatic and aromatic nitriles. When a rapid current of the fluoride is passed into acetonitrile, it is absorbed with evolution of heat, and, on cooling, colourless, deliquescent, fuming crystals, having the composition $MeCN,BF_3$, separate. The substance melts at 120°, sublimes, and may be preserved in sealed tubes containing boron fluoride. It is soluble in alcohol and ether, and with decomposition in water and alkalis. Similar compounds are formed with benzonitrile and toluonitrile. Hydrogen cyanide forms a similar very unstable compound with absorption of heat. JN. W.

Action of Ammonia on some Compounds of the Haloïd Salts of Mercury. By R. VARET (*Compt. rend.*, **112**, 1312—1314). —When a solution of mercury cadmium iodocyanide,

$$HgCy_2,CdCy_2,HgI_2,8H_2O,$$

is allowed to drop into aqueous ammonia until a permanent precipitate is formed, and the precipitate is allowed to remain in contact with the mother liquor for some time with occasional agitation, a yellowish, amorphous powder is obtained, which must be dried rapidly on filter paper. It is mixture of ammonio-cadmium iodide with the compound $HgCy_2,CdCy_2,HgI_2,4NH_3$ or its isomeride $2HgCy_2,CdI_2,4NH_3$, the ammonia having produced a reaction the inverse of that which gave rise to the original salt, and again formed cadmium iodide. Similar results are obtained by dissolving mercury cadmium iodocyanide in ammonia.

Mercury potassium iodocyanide dissolves abundantly in aqueous ammonia at 40°, and separates unchanged on cooling.

Ammonia acts slowly on mercuric cyanide, but if the moist salt is heated in a current of the gas at 100° until quite dry and the passage of the gas is afterwards continued for some time at the ordinary temperature, the compound $HgCy_2,2NH_3$ is obtained as a white, amorphous powder, which alters readily when exposed to air, losing ammonia rapidly and absorbing water.

Mercury barium chlorocyanide, under similar conditions, yields the compound $2HgCy_2,BaCl_2,4NH_3$, which alters rapidly on exposure to air, is only slightly soluble in ammonia, and is decomposed by water. The chlorocyanide absorbs ammonia much more rapidly than either of its constituent salts separately, and the compound seems to be more stable than the compound formed by either of the simple salts. C. H. B.

The Cyanogen Compounds of Magnesium. By R. VARET (*Compt. rend.*, **112**, 1449—1451).—A triple salt of the composition $MgCy_2,HgCy_2,HgI_2 + 8H_2O$ is formed when small quantities of magnesium iodide are thrown into a concentrated solution of mercuric cyanide maintained at 60—70°, using 15 grams of magnesium iodide to 25 grams of mercuric cyanide. The filtered liquid carefully evaporated on the water-bath deposits, on cooling, large, light-yellow, transparent lamellæ, which may be dried in paper. When the salt is carefully heated, it first yields hydrocyanic acid, water, and mercuric iodide, and subsequently, on fusion, an abundant sublimate of mercuric iodide and mercury, together with cyanogen. From the character of this decomposition, it is evident that the compound is more complex than would be formed by a simple union of mercuric cyanide and magnesium iodide. When a solution of the iodocyanide is boiled with ammonium picrate, the fine-red coloration of ammonium isopurpurate is produced; such a reaction does not occur with mercuric cyanide. Similarly, copper sulphate yields a precipitate of mercuric iodide and cupric cyanide, the latter further decomposing into cuprous cyanide and cyanogen. Mercuric cyanide does not react with the oxygen salts of copper.

If a concentrated solution of magnesium bromide be dropped slowly into a saturated solution of mercuric cyanide at 50°, and the mixture evaporated, white, nacreous, silky lamellæ of the formula $MgCy_2,HgCy_2,HgBr_2 + 8H_2O$ are deposited. This substance is very hygroscopic and soluble in water, and is unstable in air. Its constitution is not clearly established. W. T.

Fulminates. By H. N. WARREN (*Chem. News*, **64**, 28).—Copper fulminate, obtained by digesting a solution of silver fulminate with copper filings, when reduced by electrolysis, yielded copper, hydrocyanic acid, and ammonia in abundance, also ammonium fulminate and fulminic acid. Cuprammonium fulminate, obtained by treating copper fulminate with excess of ammonia, dried over sulphuric acid, and decomposed by hydrogen sulphide, yielded copper sulphide, carbamide, and ammonium thiocyanate. Silver fulminate, by the action of dry silicon fluoride, yielded silver fluoride and an explosive gas. By the action of chlorine, bromine, or iodine, the haloïd silver salt and chloro-, bromo-, or iodo-picrin were obtained. D. A. L.

Allyl Alcohol and its Formation from Dichlorhydrin and Sodium. By H. TORNÖE (*Ber.*, **24**, 2670—2678).—Aqueous allyl alcohol, which has been kept over freshly ignited potassium carbonate, still contains a considerable quantity of water; on repeated fractional distillation, such a mixture can be separated into two portions, boiling constantly at about 87·5° and 97° respectively. The fraction of lower boiling point seems to be a mixture of 72·3 per cent. of allyl alcohol and 27·7 per cent. of water; the fraction of higher boiling point is almost anhydrous allyl alcohol, but contains a small quantity of acraldehyde. On treating the almost anhydrous allyl alcohol with dry chlorine, a large quantity of acraldehyde is formed, and the yield of pure dichlorhydrin (b. p. 181—186°, with slight decomposition) is only about 20 per cent. of the theoretical.

Both the dichlorhydrins are very stable towards acid reducing agents, and are not acted on by nascent hydrogen or by stannous chloride; when heated with hydriodic acid and amorphous phosphorus, they both yield isopropyl iodide, and a small quantity of a liquid boiling at about 34—36°, which is most probably isopropyl chloride.

It has been previously shown by Hübner and Müller (*Annalen*, **159**, 168) that allyl alcohol is produced by the action of sodium on an anhydrous ethereal solution of dichlorhydrin (b. p. 144°); the author succeeded in isolating impure epichlorhydrin from the products of this reaction and proved its presence by converting it into dichlorhydrin.

When an anhydrous ethereal solution of epichlorhydrin is treated with sodium, only a trace of a liquid, which seems to be impure allyl alcohol, is obtained, so that it is impossible to assume that the production of allyl alcohol from dichlorhydrin, in the reaction just referred to, is due to the intermediate formation of epichlorhydrin.

The two acetylchlorhydrins are converted into one and the same allyl acetate on treatment with sodium in anhydrous ethereal solution. F. S. K.

Rotatory Power of Compounds of Mannitol with Acid Molybdates. By D. GERNEZ (*Compt. rend.*, **112**, 1360—1363).—The author has previously shown (Abstr., 1890, 744) that compounds such as active malic acid having both acid and alcoholic functions in aqueous solution form compounds with optically inert substances such as the molybdates, which compounds have a greater rotatory power than the original acid. The present paper describes similar compounds formed by the alcohol mannitol. Solutions were employed containing 0·7583 gram and 1·5866 grams of mannitol, to which were added varying quantities of the acid sodium or ammonium molybdates respectively, differing by 1/12 equivalent, and sufficient water to make the total volume 24 c.c. The initial negative rotation of the mannitol is changed to a positive rotation on the addition of the first 1/12 equivalent of acid molybdate; this rotation increases regularly on the addition of further quantities of the acid salt until maxima of 2° 45′ and 5° 16′ respectively are attained with 6·75/12 equivalent of the acid molybdate. This proportion of the acid salt corresponds with 3·9375 equivalents of molybdic acid to 1 equivalent of mannitol. The rotation observed is slightly less if the ratio be 4 to 1. As normal sodium molybdate has no action on mannitol, there is, considering only the molybdic acid not saturated by the soda, 2·25 equivalents of molybdic acid to 1 equivalent of mannitol, or 9 to 4 respectively as the proportions in the compound formed. Further additions of the salt give gradually decreasing rotations, indicating the decomposition of the compound corresponding with the maximum and a tendency towards some other state of equilibrium. W. T.

Configuration of Grape Sugar and its Isomerides. By E. FISCHER (*Ber.*, **24**, 2683—2687).—In the last paper on this subject (this vol., p. 1173), the configuration of grape sugar was expressed by the formula

$$CHO{\cdot}\underset{-}{C}H(OH){\cdot}\underset{+}{C}H(OH){\cdot}\underset{+}{C}H(OH){\cdot}\underset{+}{C}H(OH){\cdot}CH_2{\cdot}OH;$$

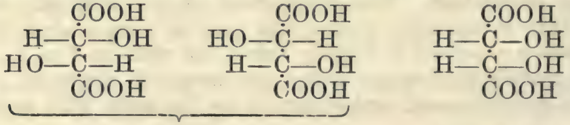
as, however, in the case of such complicated molecules, the employment of the signs + and − for denoting the arrangement in space may easily give rise to mistaken views, it becomes necessary to give a more complete explanation of the formulæ. For this purpose, the four asymmetric carbon atoms in the molecule of grape sugar may be numbered as shown below :—

$$CH_2(OH){\cdot}\overset{1}{C}H(OH){\cdot}\overset{2}{C}H(OH){\cdot}\overset{3}{C}H(OH){\cdot}\overset{4}{C}H(OH){\cdot}CHO.$$

Van't Hoff, in his general considerations, on which the author's special deductions are based, only compares the carbon atom 1 with the carbon atom 4, and 2 with 3; consequently, in the case of grape sugar, the arrangement of the hydrogen atom and the hydroxyl group around 1 is the reverse of that around 4, whilst the arrangement around 2 and 3 is the same. The arrangement of the asymmetric group around the carbon atom 1 can, however, be also compared with that of the two central asymmetric groups, as was done by the author in fixing the relationship of grape sugar to xylose and arabinose; it was then shown that the arrangement of the hydrogen atom and hydroxyl group around the carbon atom 1 is identical with that around 3. From a superficial examination, it might be concluded that this is also so in the case of the carbon atoms 1 and 2, but as a matter of fact the reverse is true.

With the aid of models, it is easily seen that, in the case of the carbon atom 2, the sign varies according as it is compared with 1 or 3. As, therefore, the above method of expressing the configuration of grape sugar is ambiguous, it is advisable to do so in another way.

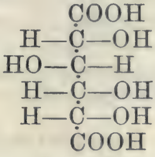
In the first place, the molecules of dextro-, levo-, and inactive tartaric acids can be constructed (with the aid of Friedländer's indiarubber models), and laid on paper in such a way that the four carbon atoms are arranged in a straight line, the hydrogen atoms and hydroxyl groups standing above the plane of the paper; the projections of these models would then be the following :—



$$\underbrace{\begin{array}{c} COOH \\ H{-}C{-}OH \\ HO{-}C{-}H \\ COOH \end{array} \qquad \begin{array}{c} COOH \\ HO{-}C{-}H \\ H{-}C{-}OH \\ COOH \end{array}}_{\text{Dextro- and levo-acids.}} \qquad \underset{\text{Inactive acid.}}{\begin{array}{c} COOH \\ H{-}C{-}OH \\ H{-}C{-}OH \\ COOH \end{array}}$$

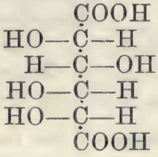
On proceeding in a similar manner with the models of d.- and l.-saccharic acids, the two following projections are obtained :—

I.



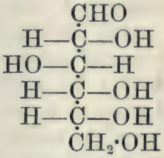
$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{COOH}\end{array}$$

II.



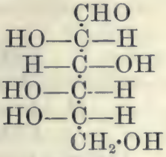
$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{COOH}\end{array}$$

As it is immaterial which of these two configurations is assigned to d.-saccharic acid, it may be assumed to have that represented by the formula I; the configurations of grape sugar and its isomerides would then be expressed as follows :—



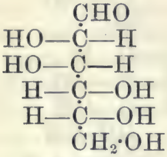
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

Grape sugar.



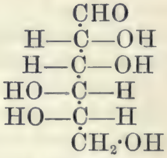
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

l.-Glucose.



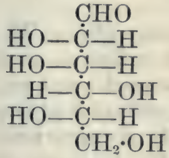
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

d.-Mannose.



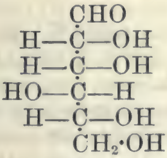
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

l.-Mannose.



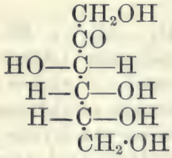
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

d.-Gulose.



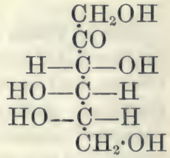
$$\begin{array}{c}\mathrm{CHO}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

l.-Gulose.



$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{CO}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

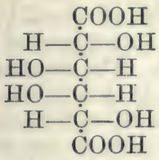
d.-Fructose.



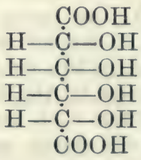
$$\begin{array}{c}\mathrm{CH_2OH}\\ \mathrm{CO}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{CH_2{\cdot}OH}\end{array}$$

l.-Fructose.

The configurations of the two inactive dicarboxylic acids of the dulcitol series, which are probably represented by mucic acid and allomucic acid, may be denoted by the following formulæ :—

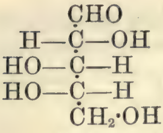


$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{H-C-OH}\\ \mathrm{HO-C-H}\\ \mathrm{HO-C-H}\\ \mathrm{H-C-OH}\\ \mathrm{COOH}\end{array}$$



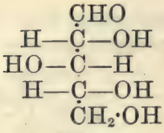
$$\begin{array}{c}\mathrm{COOH}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{H-C-OH}\\ \mathrm{COOH}\end{array}$$

This manner of expressing configuration can also be adopted in the case of the pentoses; its use is even more advantageous in the case of the more complex molecules of the heptoses, octoses, &c., where the ambiguity of the signs + and − constantly becomes greater. The configurations of the two pentoses, for example, and of the trihydroxyglutaric acids obtained therefrom, may be represented by the following projections :—



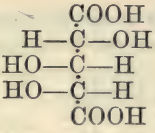
$$\begin{array}{c}CHO\\ H-C-OH\\ HO-C-H\\ HO-C-H\\ CH_2{\cdot}OH\end{array}$$

Arabinose.



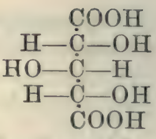
$$\begin{array}{c}CHO\\ H-C-OH\\ HO-C-H\\ H-C-OH\\ CH_2{\cdot}OH\end{array}$$

Xylose.



$$\begin{array}{c}COOH\\ H-C-OH\\ HO-C-H\\ HO-C-H\\ COOH\end{array}$$

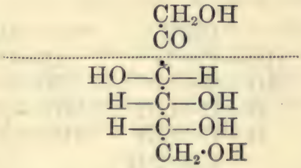
Active acid from arabinose.



$$\begin{array}{c}COOH\\ H-C-OH\\ HO-C-H\\ H-C-OH\\ COOH\end{array}$$

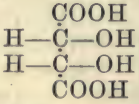
Inactive acid from xylose.

The advantage of the new formulæ is more particularly noticeable in considering those reactions in which an increase or decrease in the number of asymmetric carbon atoms takes place; as, for example, in the oxidation of levulose to inactive tartaric acid; this change is very simply expressed in the following way:—



$$\begin{array}{c}CH_2OH\\ CO\\ \hline HO-C-H\\ H-C-OH\\ H-C-OH\\ CH_2{\cdot}OH\end{array}$$

d.-Fructose.



$$\begin{array}{c}COOH\\ H-C-OH\\ H-C-OH\\ COOH\end{array}$$

Inactive tartaric acid.

F. S. K.

Stachyose. By A. v. PLANTA and E. SCHULZE (*Ber.*, **24**, 2705—2709).—Stachyose (Abstr., 1890, 1088), like raffinose, is a triose, and on inversion it yields galactose, grape sugar, and levulose; mannose and pentoses could not be detected in the solution of the inverted sugar. Since stachyose yields 37—38 per cent. of mucic acid on oxidation with nitric acid, it may be assumed that the molecule of this sugar is formed by the combination of 3 mols. of galactose either with 2 mols. of grape sugar and 1 mol. of levulose, or with 1 mol. of grape sugar and 2 mols. of levulose; it is probable, therefore, that stachyose has the molecular formula $C_{36}H_{64}O_{32}$. F. S. K.

Lupeol. By A. LIKIERNIK (*Ber.*, **24**, 2709—2710).—Lupeol (this vol., p. 551) may be considered as a homologue of α- and β-amyrin (compare Vesterberg, this vol., p. 165). The relationship of lupeol to the amyrins is shown by the fact that they all give substitution, and not additive, products with bromine; a chloroform solution of each of the three compounds turns reddish-violet on the addition of acetic anhydride and a little concentrated sulphuric acid. F. S. K.

Conversion of Starch into Dextrin by the Butyric Ferment. By A. VILLIERS (*Compt. rend.*, **113**, 144—145).—When starch paste is inoculated with the butyric ferment and kept at 40°, the rotatory power at first increases, reaches a maximum after 2½ days, and then slowly decreases, the starch almost entirely disappearing. When filtered through biscuit porcelain, and kept at 40° for several days, the rotatory power of the solutions undergoes no further change. They give no starch reaction with iodine. If a small quantity of starch is added to the sterilised solutions, and they are then kept at

40°, the starch disappears after some days, but the rotatory power of the liquid remains practically unchanged.

In the conversion of starch into dextrin by the action of the butyric ferment, the latter secretes a soluble product capable of producing the conversion in the absence of any organisms. This product is formed continually in very small quantities, and its activity seems to be exhausted almost as fast as it is formed.

C. H. B.

Bleaching of Cotton by Hydrogen Peroxide. By PRUD'HOMME (*Compt. rend.*, **112**, 1374—1376).—The superiority of the results obtained in bleaching cotton when calcined magnesia is added to the hydrogen peroxide used is due to the formation of magnesium peroxide, which is more stable than hydrogen peroxide at 100°. 6 per cent. hydrogen peroxide, diluted with 10 parts water and boiled for half an hour, has its titration value reduced to one-tenth of that shown before boiling. If calcined magnesia, to the amount of 5 per cent. of the weight of hydrogen peroxide, be added, the titration value is only reduced to nine-tenths. Magnesia is subjected to the action of 3 per cent. hydrogen peroxide for some time at the ordinary temperature, filtered, washed, and dried at 100—105°; the active oxygen, titrated with permanganate, corresponds with the formula $3Mg(OH)_2 + MgO(OH)_2$ for the dry product. This substance has an alkaline reaction, and loses all its active oxygen at about 300°. Magnesium peroxide is also formed when the metal is dissolved in hydrogen peroxide.

Zinc and cadmium also form peroxides; that of zinc has probably the formula $2ZnO + ZnO(OH)_2$.

Hydrogen peroxide has a direct action not only on the various colouring matters present, but even on such substances as cellulose. Fatty substances give off much carbonic anhydride on boiling with hydrogen peroxide, due to the oxidation of the glycerol set free by the saponification brought about by the magnesia employed in the process. Slightly acid hydrogen peroxide attacks neutral fats on boiling, liberating fatty acids and disengaging carbonic anhydride. Under the joint action of magnesia and hydrogen peroxide, the fatty acids are oxidised with production of carbonic anhydride. Oleïc acid is, under these conditions, partially transformed into palmitic acid, just as when treated with caustic potash.

In bleaching by hydrogen peroxide, cellulose is converted into oxycellulose, recognised by dyeing with basic colouring matters which fix on oxycellulose without a mordant. The alteration of cellulose is greater if impregnated with concentrated caustic soda before treating it with hydrogen peroxide.

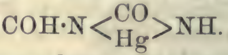
This action of hydrogen peroxide is greatly augmented by the presence of metallic oxides, which appear to serve as vehicles for the active oxygen; the bleaching, therefore, should be preceded by treatment with a very dilute acid. A piece of cloth mordanted with iron, chromium, and aluminium, and boiled for one or two hours with magnesia and hydrogen peroxide, is strongly attacked in the mordanted portions. The action of hydrogen peroxide on cellulose presents great analogies with that of cuprammonium solutions, which also act as oxidising agents, forming oxycellulose.

Cotton cloth treated with caustic soda at 36° and thoroughly washed is acted on more strongly by cuprammonium solutions of moderate concentration than cloth not so treated. It is concluded that, contrary to the received opinion, cellulose is attacked and suffers transformation under the action of Schweitzer's reagent.

W. T.

Ureides from Normal Acids. By C. MATIGNON (*Compt. rend.*, **112**, 1367—1369).—The heats of combustion of formylcarbamide and acetylcarbamide are respectively +207·3 Cal. and +360·9 Cal.; the corresponding heats of formation are +119·3 Cal. and +129 Cal.

In accordance with the difference, 153·6 Cal., between the heats of combustion of these two successive homologues, there is great similarity in their reactions with the same reagents. Formic and acetic acids differ considerably in properties, and the difference between the heats of combustion of these acids taken in the solid state is only 140 Cal.

Formic acid and urea in solution combine with liberation of +13·4 Cal., whereas acetylcarbamide is not formed from acetic acid and urea in solution, as the reaction would require an absorption of 0·2 Cal. The synthesis of acetylcarbamide from acetamide and urea has not been accomplished; it would require an absorption of 12·5 Cal. Acetylcarbamide and formylcarbamide yield flocculent precipitates with mercuric chloride and potash. The formula of the compound with formylcarbamide is probably  $COH\cdot N<^{CO}_{Hg}>NH$.

Urea acetate, $CON_2H_4,C_2H_4O_2 + 2H_2O$, forms large, deliquescent crystals; the heat of solution at 16° is −8·8 Cal. at a concentration of $\frac{1}{8}$ mol. per litre. Its heat of formation is +3·1 Cal.; the smallness of this number accounts for the easy dissociation of the salt by water.

W. T.

Products of Oxidation of Uric Acid. By C. MATIGNON (*Compt. rend.*, **112**, 1263—1266).—*Allantoïn.*—Heat of combustion at constant pressure, +413·8 Cal.; heat of formation, +170·4 Cal.; heat of dissolution at 15°, −7·5 Cal.

Alloxan.—Heat of combustion, +278·5 Cal.; heat of formation, +236·7 Cal.; heat of dissolution, +4·1 Cal., −4·2 Cal., and −9·0 Cal. in the three states of hydration respectively.

Alloxantin.—Heat of combustion, +586·3 Cal.; heat of formation, +513·1 Cal.; heat of dissolution at 15°, −9 Cal.

$C_4O_4N_2H_2$ sol. + H_2O sol. = $C_4O_5N_2H_4$ develops +9·0 Cal.
$C_4O_5N_2H_4$ sol. + $3H_2O$ sol. =
$C_4O_5N_2H_4,3H_2O$ sol................ „ +6·9 Cal. (3 × 2·3).

It follows that the entrance of the first molecule of water into the molecule of alloxan causes a development of heat almost as great as the heat of hydration of phosphoric anhydride, and this result confirms

Baeyer's view, that the compound $C_4O_4N_2H_2$ is the anhydride of alloxan.

$C_5O_3N_4H_4$ sol. + O gas + H_2O liq. = $C_4O_3N_4H_6$ diss. + CO_2 gas .... develops +40·1 Cal.
$C_5O_3N_4H_4$ sol. + O gas + $2H_2O$ liq. = $C_4O_5N_2H_4$ diss. + CON_2H_4 diss. .... „ +23·7 „

It would seem, therefore, that the oxidation of uric acid should always produce allantoïn, and this is true so long as no secondary reaction takes place with the same velocity as the principal reaction; for example, when potassium permanganate is the oxidising agent. If, on the other hand, nitric acid is the oxidising agent, nitrous acid is formed, and this at once attacks the urea, and the heat developed by this simultaneous secondary reaction is sufficient to turn the balance in favour of alloxan. The thermochemical results explain the well-known fact that the action of oxidising agents on uric acid yields either allantoïn or alloxan, but never both at the same time.

C. H. B.

Parabanic and Oxaluric Acids. By C. MATIGNON (*Compt. rend.*, **113**, 198—200).—*Parabanic Acid.*—Heat of combustion, +212·7 Cal.; heat of formation, +139·2 Cal.; heat of dissolution at 20°, −5·1 Cal.

Oxaluric Acid.—Heat of combustion, +211 Cal.; heat of formation, +209·9 Cal.

The formation of parabanic acid from oxalic acid and urea would develop +2·2 Cal., and the formation of oxaluric acid would develop +2·5 Cal. These numbers are very low, and explain the difficulty of passing directly from urea to the ureides. The conversion of parabanic acid into oxaluric acid by elimination of water would develop only +0·3 Cal.

A cold solution of potassium hydroxide, containing 1 gram-molecule in 20 litres, rapidly converts both parabanic acid and oxaluric acid into normal potassium oxalate, the change in the case of parabanic acid being accompanied by the development of +24·4 Cal., the acid being solid and the potash and the products dissolved. The heat of formation deduced from this result is 138·7 Cal., whilst the direct determination gives 139·2 Cal.

Potassium oxalurate, prepared by dissolving oxaluric acid in an equivalent quantity of potash solution and evaporating the liquid, is different from the oxalurates described by Menschutkin and Strecker respectively. It crystallises in stellate groups of slender, anhydrous, prismatic needles.

$C_3O_4N_2H_4$ sol. + KOH sol. = $C_3O_4N_2H_3K$ sol. + H_2O sol. .... develops +30·2 Cal.

The action of the first equivalent of potash on oxalic acid develops +34·2 Cal.

C. H. B.

Action of Diazobenzene Chloride on Acetone. By E. BAMBERGER and P. WULZ (*Ber.*, **24**, 2793—2797).—A study of the properties of a hydronaphthol obtained from tetrahydronaphthylene oxide (this vol., p. 1073) led Bamberger to the conclusion that compounds containing the radicle $CH_2\cdot CO$ (or $CH\colon CH\cdot OH$), whether belonging to the fatty or the aromatic series, must be capable of forming colouring matters on treatment with diazotised bases in the presence of alkalis. This opinion has been verified with acetone, acetaldehyde, propaldehyde, œnanthaldehyde, acetophenone, camphor, &c., all of which give intense, dark claret coloured solutions. Formaldehyde, which does not contain the radicle, does not give the reaction, but, on the other hand, substances like lactic acid and dextrose, and, in particular, ethylenic compounds, such as allyl alcohol, dihydronaphthalene, dihydrobenzaldehyde, &c., form colouring matters under the conditions named.

When a mixture of acetone (12 grams) with a solution of diazobenzene chloride (prepared from 18·6 grams aniline) is slowly stirred into carefully cooled 20 per cent. aqueous soda (200 grams), a red coloration is produced, and the mixture becomes turbid, finally depositing a brownish-black resin. The product can be obtained in a crystalline form by dissolving it in well-cooled sulphuric acid, and, after 12 hours, pouring the deep blue solution on to ice, drying the reddish-brown, flocculent precipitate, and then carefully extracting with ether. On evaporating the deep red ethereal solution, a crystalline residue is obtained which can be purified by repeated crystallisation from alcohol. The compound has the composition $C_{15}H_{14}N_2O$, and is more probably a bis-hydrazone of mesoxalaldehyde than a disazo-derivative of acetone. It crystallises either in lustrous, garnet-red prisms, showing an intense, steel-blue, metallic shimmer, or by rapid crystallisation in tufts of flat needles, melts at 134—135°, and dissolves easily in the ordinary organic solvents, but only very sparingly in water. It has feebly basic properties, and dissolves in concentrated mineral acids, forming deep violet-blue solutions, from which the colouring matter is precipitated unchanged on the addition of water. The compound is destitute of tinctorial power, but its sulphonic acid, contained in the aqueous solution after extraction with ether, dyes wool and silk a bright chestnut-brown in an acid bath.

In the concluding portion of the paper, the authors draw attention to the difference between this reaction and that employed by Penzoldt and Fischer for the detection of aldehydes (Abstr., 1883, 829).

W. P. W.

Ethereal Nitrosocyanacetates. By P. T. MULLER (*Compt. rend.*, **112**, 1372—1373).—These salts are prepared by the action of amyl nitrite on the sodium derivatives of ethereal cyanacetates, with subsequent treatment of the sodium salts produced with sulphuric acid.

Ethyl Nitrosocyanacetate.—An equivalent quantity of sodium dissolved in absolute alcohol is added, little by little, to ethyl cyanacetate (1 mol.), and amyl nitrite (1 mol.) is added, in small portions at a time, to the resulting mass, which is then heated to 50—60°. It is cooled, washed with ether, and precipitated with dilute sulphuric acid. The oil is dissolved in ether, dried, and crystallised by evaporation. Ethyl nitrosocyanacetate, $NO\cdot CH(CN)\cdot COOEt$, forms small, white crystals, melts at 127—128°, and is very soluble in water, alcohol, and ether, less so in benzene. The sodium salt crystallises in small, yellow, fibrous prisms containing 5 mols. H_2O. It is formed directly by the action of amyl nitrite on ethyl sodiocyanacetate; the product is evaporated to dryness and dissolved in alcohol; the salt is precipitated by the addition of benzene.

Methyl nitrosocyanacetate is obtained, by the same method as its homologue, in the form of small, tabular crystals melting at 119°. The sodium salt occurs in yellow, flat prisms containing $1\frac{1}{2}$ mols. H_2O.

W. T.

Cyanostearic Acid, Hexadecylmalonamic Acid, and Hexadecylmalonic Acid. By C. HELL and J. SADOMSKY (*Ber.*, **24**, 2778—2785).—*α-Cyanostearic acid*, $CN{\cdot}C_{17}H_{34}{\cdot}COOH$, is prepared by dissolving ethyl α-bromostearate (this vol., p. 1336) (50 grams) in alcohol, adding potassium cyanide (14 grams) dissolved in the smallest quantity of hot water, and heating the mixture in a reflux apparatus for 5—6 days, then collecting the dark precipitate, washing with alcohol, dissolving in water, adding sulphuric acid, filtering from the humus substance which separates, extracting with ether, and finally purifying the acid by crystallisation from glacial acetic acid, and subsequently from a mixture of alcohol and light petroleum; it forms small, iridescent, transparent plates or prisms, melts at 83·5°, and is readily soluble in alcohol, ether, and glacial acetic acid, but almost insoluble in light petroleum. When the acid is heated at 200—250°, carbonic anhydride is evolved and stearonitrile (Krafft and Stauffer, Abstr., 1882, 1274) is formed.

Hexadecylmalonamic acid, $CONH_2{\cdot}C_{17}H_{34}{\cdot}COOH$, is obtained by boiling α-cyanostearic acid with alcoholic potash for 2—3 days, distilling off the alcohol, dissolving the residue in water, precipitating with hydrochloric acid, redissolving in ether, and crystallising the plates which first separate from the ethereal solution from a mixture of light petroleum and a little alcohol. The acid forms delicate, silky scales, and is readily soluble in hot alcohol, ether, and hot benzene, but only sparingly in light petroleum; it begins to decompose below its melting point into stearamide (m. p. 108°), and when heated at 130—150°, it is completely converted into the latter.

Hexadecylmalonic acid, $C_{17}H_{34}(COOH)_2$, is formed by boiling hexadecylmalonamic acid with alcoholic potash for 3—4 days, or α-cyanostearic acid with an excess of the latter for 6—7 days, isolating in the same manner as hexadecylmalonamic acid, and finally crystallising from glacial acetic acid; it crystallises in lustrous, pointed, rhombic tablets, melts at 121·5—122°, and is readily soluble in alcoholic ether, hot benzene, or glacial acetic acid, but almost insoluble in light petroleum, and quite so in water. The acid is identical with the cetylmalonic acid described by Guthzeit (Abstr., 1881, 408). When heated at 160—180°, hexadecylmalonic acid is converted into stearic acid with the evolution of carbonic anhydride. The salts likewise decompose on heating, as follows: the *barium salt* at 270—290°, the *cadmium salt* at 250°, the *zinc* salt at 230°, the *copper salt* at 210°, and the *silver salt* at 190°.

A. R. L.

Acids from Baku Petroleum. By O. Aschan (*Ber.*, **24**, 2710—2724; compare Abstr., 1890, 737).—Heptanaphthenecarboxylic acid, $C_8H_{14}O_2$, has been previously isolated by Markovnikoff; it boils at 237—239°, and is with difficulty rendered anhydrous. The coefficient of refraction for sodium light is $N = 1\cdot4486$, and the molecular refractive power $= 38\cdot7$, which agrees with the theory. The acid is unaffected by bromine or potassium permanganate. The *methyl salt* boils at 190—192°; the specific gravity $= 0\cdot9357$, 18°/18°. The *potassium* and *sodium salts* are crystalline and readily soluble in water or alcohol. The *calcium salt*, $(C_7H_{13}CO\cdot O)_2Ca$, crystallises from water in long needles, and is deposited in an amorphous condition on heating a cold, saturated solution. The *barium salt* is obtained in anhydrous, lustrous plates; the *silver salt* is amorphous. All these compounds resemble the corresponding hexanaphthenecarboxylates in general properties. The *chloride*, $C_7H_{13}\cdot COCl$, is a strongly refractive, dense liquid, which boils at 193—195° and gradually undergoes decomposition. The *amide*, $C_7H_{13}\cdot CONH_2$, is most readily prepared by heating the acid (5 parts) with ammonium thiocyanate (4 parts) until a portion becomes crystalline on cooling; it is deposited from a mixture of ether and light petroleum in silvery, lustrous plates; it melts at 133°, but sublimes below 100°, and boils at about 250° with slight decomposition. The compound is somewhat volatile with steam, and combines with hydrochloric acid and calcium chloride. The *nitrile*, $C_7H_{13}CN$, is formed by the distillation of the preceding compound; it boils at 199—201° (corr.) and has a characteristic smell; the coefficient of refraction is $[n]_D = 1\cdot4452$.

Heptanaphthenamine, $C_7H_{13}\cdot NH_2$, is readily prepared from the amide by Hofmann's method; the yield is 66 per cent. of theory. It boils at 151—153° (corr.), and is a colourless liquid, absorbing carbonic anhydride from the atmosphere, and giving the ordinary reactions for primary amines. The *hydrochloride* forms large, lustrous plates, which are excessively soluble in water or alcohol, and are very hygroscopic; the *platinochloride* crystallises in large, lustrous, golden, hexagonal plates. Attempts to prepare heptanaphthene alcohol by means of the diazo-reaction were not very successful; a liquid was obtained which boiled at 161—163°: it was, however, coloured, and contained nitrogen.

Heptanaphthenecarboxylic acid is oxidised on boiling with 10 parts of nitric acid (sp. gr. 1·3); acetic acid, carbonic anhydride, and oxalic acid are formed, together with a viscid, uncrystallisable liquid, which is readily soluble in water and which appears to be a polybasic hydroxy-acid; the *silver salt* contains, as the mean of several analyses, 61·12 per cent. of silver. By the prolonged action of phosphorus and hydriodic acid on heptanaphthenecarboxylic acid at 200—240°, a hydrocarbon is obtained which boils at 117—118°, and is identical with the octonaphthene, C_8H_{16}, isolated by Markovnikoff from Caucasian petroleum. The yield is 29 per cent. It thus appears that the naphthene acids are simply monocarboxylic acids of the naphthenes. This portion of the paper concludes with some polemical remarks on a recent communication of R. Zaloziecki, respecting the constitution of petroleum acids (compare this vol., p. 999).

Octonaphthenecarboxylic acid, $C_9H_{16}O_2$, has been previously described by Markovnikoff; it boils at 251—253° (corr.), and has a sp. gr. = 0·9893, 0°/0°; its coefficient of refraction is $[n] = 1{\cdot}453$, and the molecular refractive power = 43·0. The *methyl salt* boils at 211—213° and is very hygroscopic. The *barium* and *calcium salts* are not decomposed by carbonic anhydride; the former is crystalline and sparingly soluble in cold water, but readily dissolves in alcohol. The *chloride* is a dense, oily liquid, which boils at 206—208° and slowly decomposes in presence of water. The amide crystallises from a mixture of benzene and light petroleum in large, thin, lustrous plates, and melts at 128—129°. J. B. T.

Propylideneacetic Acid. By P. Ott (*Ber.*, **24**, 2600—2604).—Propylideneacetic acid is obtained by warming equal weights of malonic acid and propaldehyde with half the weight of acetic acid on the water-bath as long as carbonic anhydride is evolved. The reaction usually takes from 3 to 4 days. The mixture is then fractionally distilled; the fractions boiling at 180—200° and 200—220° contain the greater part of the product. From former experiments, the product is known to be a mixture (this vol., p. 821); it was worked up as follows:—The fraction boiling at 180—200° is neutralised with barium carbonate, evaporated to dryness, and extracted with absolute alcohol until quite white. It is then dissolved in water, the solution evaporated until a crust separates, which dissolves on cooling, and to the clear cold solution alcohol is added until a considerable portion of the salt is precipitated. The precipitate is then dissolved by heating the mixture, and, on cooling, the barium salt separates in large, nacreous leaves. *Barium propylideneacetate* crystallises without water, is very characteristic, is insoluble in absolute alcohol, easily soluble in water, and more so in cold than in hot water. Pure propylideneacetic acid is obtained by decomposing the above salt with hydrochloric acid, and extracting with ether. It has an odour somewhat like that of crotonic acid, is quite colourless, boils at 193·5°, and is sparingly soluble in cold water. The *calcium* salt crystallises with 1 mol. H_2O, is more soluble in cold water than in hot, and crystallises in beautiful needles on heating the cold saturated solution in a sealed tube. It is easily soluble in cold water, less readily in absolute alcohol, and separates from the latter in aggregates of small needles.

On examining the mother liquors of the crude barium propylideneacetate, the authors separated a salt which they identified as barium ethylidenepropionate; and they point out that this explains the formation of a small quantity of lactone, observed by Zincke and Küster on boiling the bromovaleric acid obtained from their propylideneacetic acid with water.

The authors have also prepared the dibromides from the three isomeric acids, allylacetic acid, ethylidenepropionic acid, and propylideneacetic acid.

Dibromallylacetic acid is easily obtained solid, melts at 58°, is easily soluble in carbon bisulphide, more sparingly in petroleum, and crystallises from the latter in small, lustrous leaflets.

The dibromides from the other two isomerides were at first oils; but after some time the dibromide from ethylidenepropionic acid solidified, and on adding a crystal of this to the dibromide from propylideneacetic acid it also solidified. Both dibromides crystallise in large, broad needles from carbon bisulphide, and in large, measurable prisms from petroleum. They both melt at 64—65°, and are identical in crystalline form and in all other properties. E. C. R.

Polymerides of Ricinoleïc Acid. By SCHEURER-KESTNER (*Compt. rend.*, **113**, 201—203).—Castor oil, when heated with water at 150°, splits up into glycerol and a mixture of rincinoleïc and diricinoleïc acids in about equal molecular proportions. The degree of polymerisation increases with the temperature, the molecular weight of the acid being 709 after heating at 200°. As the molecular weight increases, the energy of the acid function decreases, diricinoleïc acid showing a feeble neutralising power. The polyricinoleïc acids are depolymerised when heated with sodium hydroxide solution at a temperature above 100°, but very little change takes place below 100°.

When ricinoleïc acid is heated alone, it gradually polymerises, and finally yields pentaricinoleïc acid with a molecular weight of 1418. C. H. B.

Solid Product of the Oxidation of Drying Oils. By A. LIVACHE (*Compt. rend.*, **113**, 136—139).—When the product of the oxidation of drying oils is placed in various solvents there is no apparent action, but after prolonged contact the product becomes more transparent and swells up, whilst at the same time the liquid becomes coloured. These phenomena are best seen when benzene is used. If the oxidised oil is triturated with one of the solvents, it rapidly swells up and becomes so finely divided that it forms a paste. If an excess of solvent is added, the particles composing the paste quickly become suspended in it. By trituration with successive quantities of the solvent until the latter no longer becomes coloured, the substance is separated into two parts, one soluble and coloured, the other insoluble, transparent, and gelatinous. If the gelatinous matter is allowed to dry, it forms an elastic and readily friable solid. When the solvent is allowed to evaporate, it leaves a sticky residue which welds at low temperatures. It is evident that the product of the oxidation of drying oils is very similar to caoutchouc. Solvents separate both of them into an insoluble and a soluble portion, and if the liquid is allowed to evaporate, the dissolved matter acts as a cement and forms a residue that is seemingly homogeneous. Oxidised oil can be prepared in large quantities by allowing oil to drop on sheets of cloth hung vertically, so that a very thin layer is exposed to the action of the air, oxidation taking place more rapidly if the room containing the cloths is heated. When the oxidised oil is triturated with a solvent and the solvent is allowed to evaporate, a residue is obtained that may be used in place of indiarubber for many purposes. C. H. B.

Preparation of Lactic Acid. By G. JACQUEMIN (*Bull. Soc. Chim.*, [3], 5, 294—298).—A wort is made by mashing malt at 50° and completing the exhaustion at successive temperatures of 60°, 63°, and 65°; finally the wort is boiled, cooled to 45°, and a carbonate is added with the pure lactic ferment. Pure cultivations of the latter are made in barley wort to which calcium carbonate is added. The fermentation is carried out in vessels which are maintained at 45° by means of steam coils or hot-water pipes; the vessel should either be hermetically closed and furnished with a gas siphon, or covered with a double cloth in order to allow the escape of carbonic anhydride and prevent entrance of dust; a tube is also arranged by which filtered air is introduced to the base of the vessel once or twice during the day in order to agitate the liquor. The fermentation is complete after a lapse of five or six days.

The resulting solution of calcium lactate is freed from nitrogenous matters by the addition of tannic acid or of a tannin extract, and crystalline calcium lactate is obtained on evaporation of the filtrate. T. G. N.

Dehydracetic Acid. By D. TIVOLI (*Gazzetta*, **21**, 414—420).—When a mixture of dry dehydracetic acid (50 grams) and lime (250 grams) is distilled, a brown oil (20 grams) is obtained, which on redistillation from lime and fractionation yields acetone, mesityl oxide, and parametaxylenol, $C_6H_3Me_2{\cdot}OH$, melting at 62·5° and boiling at 225° (compare Abstr., 1878, 411; 1884, 737).

The formation of an aromatic compound directly from dehydracetic acid, in this manner, being difficult to understand, the author suggests that the xylenol may be a condensation product of the acetone. By the action of lime on acetone, Fittig (*Annalen*, **110**, 32; **112**, 311) obtained a substance melting at 28° and boiling at 210—220° to which he assigned the formula $C_9H_{14}O$, and the name phorone. The author, on preparing this substance, only obtained it in very small quantity, but suspects it to be xylenol. W. J. P.

Homologues of Malic Acid. By A. MICHAEL and G. TISSOT (*Ber.*, **24**, 2544—2546).—In a recent paper, Bischoff states that Fittig has obtained ethylmethylmaleïc anhydride by the action of pyruvic acid on pyrotartaric acid. The authors, in the course of their work on the homologues of malic acid, have also obtained this compound synthetically, and therefore communicate part of their results, although the investigation is not yet completed.

In order, first of all, to settle the question of the constitution of citramalic acid, the authors have prepared methoxysuccinic acid, which, according to Morris (Abstr., 1880, 6) and Bredt (Abstr., 1882, 162), is not identical with the first-named acid. They find, contrary to Bredt's statement, that the acid may be readily obtained by the action of nascent hydrogen cyanide on ethyl acetoacetate, and that it melts at 119° instead of 106°. Citramalic acid prepared by Morawski's method also melted at 119°, and behaved in exactly the same manner as methoxysuccinic acid, so that the two acids must be identical.

Symmetrical ethylmethylmalic acid may be readily obtained in a similar manner from ethyl ethylacetoacetate, and forms hygroscopic prisms, melts at 132°, and yields well crystallised salts. When heated, it passes almost quantitatively into ethylmethylmaleïc anhydride, which boils without decomposition at 226°, dissolves only slightly in water, and yields salts of ethylmethylmaleïc acid with alkalis. On the addition of acids to aqueous solutions of the salts, the anhydride is reprecipitated as an oil.

Pyrocinchonic anhydride may be obtained in like manner from ethyl methylacetoacetate, and the authors are at present engaged on the further investigation of this compound. They also find that the β-γ-dicarboxyl-γ-valerolactone described by Rach (Abstr., 1886, 1012) may be readily obtained from the products of the hydrolysis of the cyanhydrin of ethyl acetosuccinate, and that the tribasic potassium salt obtained by boiling it with potash loses water on heating at 150° in a vacuum, forming an acid which may be identical with cinchonic acid. H. G. C.

Thermochemistry of Humic Acid from Sugar. By BERTHELOT and ANDRÉ (*Compt. rend.*, **112**, 1237—1245).—Humic acid from sugar (this vol., p. 1089), prepared by separation from its alkali salts, and dried rapidly at a low temperature, had a composition agreeing with the formula $2C_{18}H_{16}O_7 + C_{18}H_{14}O_6$. Its heat of combustion was 5880 cal. at constant volume; consequently the heat of formation at constant pressure is 731 cal. for 1 gram. If the oxygen united with the hydrogen to form water, and the latter combined with the carbon and the surplus of hydrogen, the formation of the humic acid would absorb 628 cal.

$C_{18} + H_{16} + O_7 = C_{18}H_{16}O_7$ ...... develops $+265{\cdot}9$ Cal.
$H_{14} + O_7 = 7H_2O$ .... ,, $+483{\cdot}0$,,
$C_{18} + H_2 + 7H_2O = C_{18}H_{16}O_7$ .... absorbs $-217{\cdot}1$,,

Now $C_6 + C_6H_2O = C_6H_{12}O_6$ absorbs $-109{\cdot}1$ Cal., and hence the conversion of $3C_6H_{12}O_6$ into $C_{18}H_{16}O_7$ is accompanied by the liberation of about $+110$ Cal.

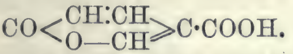
Humic acid dried at about 100° swells up, forms a pasty mass in contact with water, but dissolves to a very slight extent only. There is, however, a considerable development of heat; $C_{18}H_{14}O_6 + H_2O = C_{18}H_{16}O_7$ develops $+13{\cdot}7$ Cal., the heat of hydration of acetic anhydride being $+13{\cdot}9$. It is remarkable that the acid tends to lose water and pass into the anhydride even at the ordinary temperature.

Humic acid is tribasic; neutralisation by the first equivalent of potassium hydroxide develops $+18$ Cal., and the salt formed is insoluble and highly stable. Addition of a second and third equivalent of alkali develops a further quantity of $+6$ Cal., with formation of bibasic and tribasic salts. Freshly precipitated humic acid, when left in contact with its mother liquor, rapidly passes into the same condition as the air-dried acid.

Humic compounds, similar to those which exist in soils, attain their maximum degree of hydration in presence of alkalis, being dehydrated in presence of acids. C. H. B.

A Furfurallevulinic Acid. By A. LUDWIG and E. A. KEHRER (*Ber.*, **24**, 2776—2778).—When a solution of levulinic acid (23·2 grams) in water (300 c.c.) and one of sodium hydroxide (16 grams) in water (160 c.c.) are successively added to furfuraldehyde (19·2 grams) dissolved in 99 per cent. alcohol (200 c.c.), and the mixture is heated for five minutes at 60°, then cooled with ice and carefully acidified with hydrochloric acid, a precipitate is produced which is found to consist of a crystalline and a pulverulent compound; these are mechanically separated. The former is purified by crystallisation from hot ether, and forms faintly yellowish-coloured prisms, having the composition of a *furfurallevulinic acid*, $C_{10}H_{10}O_4$; it is very sparingly soluble in cold water and boiling light petroleum, readily soluble in hot alcohol or ether, and very easily in chloroform and benzene. The *silver salt*, $C_{10}H_9O_4Ag$, is not very sensitive towards light; the *calcium salt*, $(C_{10}H_9O_4)_2Ca + 2H_2O$, crystallises in yellow needles. The acid melts at 113° without perceptible decomposition, but after resolidification at 8—9° lower, having in fact then the same melting point as the above-mentioned pulverulent compound, which appears to be an isomeride, and seems also to be produced when the furfurallevulinic acid is crystallised from boiling water; this may be due to the fact that in the latter operation the acid melts prior to dissolving. Further experiments are in progress. A. R. L.

Decomposition Products of α-Hydroxy-acids. By H. v. PECHMANN (*Annalen*, **264**, 261—309).—An exhaustive investigation of coumalinic acid, a compound obtained by treating malic acid with concentrated sulphuric acid (compare Abstr., 1884, 1124), has proved conclusively that it is a derivative of an unsaturated lactone (coumalin), and that its constitution is expressed by the formula



$$CO<\begin{matrix}CH:CH\\O—CH\end{matrix}>C\cdot COOH.$$

Coumalinic acid is best prepared by heating anhydrous malic acid (50 grams) on the water-bath with a mixture of concentrated sulphuric acid (75 grams) and 10—12 per cent. anhydrosulphuric acid (75 grams); when the evolution of carbonic oxide ceases, which is usually the case in 1½—2 hours, the solution is carefully mixed with ice (200 grams), kept over night, the precipitated acid separated by filtration, washed with ice-cold water until almost free from sulphuric acid, and then dried on porous plates; the acid in the mother liquors and washings is extracted by shaking six times with ether. The total yield of the crude product is about 80 per cent. of the theoretical, but it contains fumaric acid and traces of trimesic acid; it can be purified by dissolving it in water at 70—80°, shaking the solution with animal charcoal, and then extracting the acid with ether. It crystallises from methyl alcohol and glacial acetic acid in colourless prisms, turns reddish at 200°, and melts at 205—210° with decomposition; it boils at about 218° under a pressure of 120 mm. with partial decomposition, and when heated carefully it gives a sublimate the edges of which have a characteristic rose-colour. It is insoluble in chloroform, benzene, and light petroleum, and only sparingly soluble in cold water, ether, acetone, and ethyl acetate, but moderately easily in methyl alcohol, glacial acetic acid, and alcohol;

its solution in water and dilute acids undergoes decomposition on boiling, with evolution of carbonic anhydride and formation of crotonaldehyde, the solution turning brown. When boiled with barium hydroxide, it is decomposed into formic acid and glutaric acid (m. p. 132—134°). It is decomposed by cold alkalis, and it reduces Fehling's solution and ammoniacal silver nitrate solution (in presence of soda) on boiling; with boiling acetic anhydride, it gives an intense, brownish-red coloration. Small quantities of coumalinic acid are most easily detected by converting the acid first into the methyl salt, and then into the characteristic anil (m. p. 140°) previously described (*loc. cit.*); this reaction can be carried out with as small a quantity as 0·02 gram of the acid, if it is not very impure. All the salts of coumalinic acid are decomposed on boiling with water, yielding a carbonate and crotonaldehyde. The *magnesium* salt, $(C_6H_3O_4)_2Mg + 6H_2O$, crystallises from warm water in colourless prisms; the *zinc* salt ($+ 6H_2O$) also crystallises very well. The *barium* salt, $(C_6H_3O_4)_2Ba + 2H_2O$, is a slightly coloured, crystalline powder, more readily soluble than the salts just described. The *silver* salt is colourless, but turns black on exposure to light in a dry condition. The *mercurous* salt is a colourless, granular compound. The salts of the alkalis are very readily soluble in water, but more sparingly in alcohol. A 5 per cent. solution of the barium salt gives precipitates with ferric chloride and with bismuth nitrate, but not with solutions of copper, cadmium, lead, manganese, or mercuric salts. The methyl salt (*loc. cit.*) boils at 178—180° under a pressure of 60 mm., and at 250—260° under the ordinary atmospheric pressure without appreciable decomposition; it crystallises well from hot water, &c., melts at 73—74°, and is decomposed by water and alkaline carbonates (see below). The *ethyl* salt, $C_6H_3O_4Et$, prepared by treating the acid with alcohol and sulphuric acid, melts at 36°, boils at 262—265°, and resembles the methyl salt in its behaviour with solvents; when treated with aniline, it is converted into a yellow, crystalline *anil*, which melts at 121°. The *chloride*, $C_5H_3O_2 \cdot COCl$, is formed when crude coumalinic acid is moistened with phosphorus oxychloride, and then warmed with phosphorus pentachloride on the water-bath, an energetic reaction taking place; it boils at about 180° under a pressure of 80 mm., and the distillate solidifies on cooling to a mass of crystals, which could not, however, be obtained free from phosphorus.

The formation of coumalinic acid from malic acid is due to the intermediate production of formylacetic acid; this is proved by the fact that ethyl sodioformylacetate (compare Wislicenus, Abstr., 1888, 129) is readily converted into coumalinic acid on treatment with concentrated sulphuric acid. The sodium derivative just referred to is without doubt a derivative of ethyl formylacetate, as, when treated with resorcinol in presence of sodium ethoxide, it yields umbelliferon, just as resorcinol and ethyl acetoacetate give β-methylumbelliferon.

β-Nitrosopropionic acid (*oximidoformylacetic acid*),

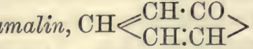
$$NOH{:}CH \cdot CH_2 \cdot COOH,$$

is obtained when dilute (1 : 5) soda (140—150 c.c.) is gradually added to a well-cooled mixture of coumalinic acid (20 grams), hydroxylamine hydrochloride (20 grams), and water (100 c.c.), and the solution then carefully warmed on the water-bath for 10—20 minutes; after cooling, sulphuric acid is added until the solution colours tropæoline paper violet, and the product is then extracted with ether. It separates from ether in colourless crystals, melts at 117—118° with decomposition, and is readily soluble in water and alcohol, but only sparingly in ether, and insoluble in chloroform, benzene, and light petroleum; it is decomposed by sodium carbonate and by boiling water, with evolution of carbonic anhydride, and it reduces Fehling's solution and ammoniacal silver nitrate solution on warming. In its aqueous solution, copper acetate produces a light-blue, crystalline precipitate, and ferric chloride a reddish-brown coloration; when warmed with acetic chloride in ethereal solution, it is converted into a compound which crystallises in colourless prisms, melts at 144—145° with decomposition, and gives a wine-red coloration with an alcoholic solution of ferric chloride. When the acid is kept for a long time, it is transformed into a porous, hygroscopic substance, which is insoluble in ether and alcohol. The molecular weight of β-nitrosopropionic acid was determined by Raoult's method, and found to be in accordance with the molecular formula given above; that it has the constitution assigned to it is proved by the following facts:—1. When boiled with dilute sulphuric acid, it is decomposed into hydroxylamine, acetaldehyde, and carbonic anhydride. 2. On reduction, it is converted into β-amidopropionic acid (β-alanine), which can be easily isolated in the form of the sulphone described below.

The most plausible explanation of the formation of β-nitrosopropionic acid from coumalinic acid is that the latter is first converted into formylglutaconic acid, $COOH\cdot CH\colon CH\cdot CH(CHO)\cdot COOH$, by direct combination with 1 mol. H_2O; this hypothetical intermediate product probably undergoes intramolecular change into a compound of the constitution $COOH\cdot CH_2\cdot CH\colon C(CHO)\cdot COOH$, which is then decomposed into 2 mols. of formylacetic acid by combination with a second molecule of water.

Benzenesulphone-β-alanine, $SO_2Ph\cdot NH\cdot CH_2\cdot CH_2\cdot COOH$, is obtained when β-nitrosopropionic acid is reduced with sodium amalgam, and the crude product shaken with soda and benzenesulphonic chloride; it crystallises from water in colourless plates or prisms, melts at 111—112°, and is readily soluble in most ordinary solvents except cold water.

Methyl dihydrogen trimesate, $C_{10}H_8O_6$, is easily obtained by treating methyl coumalinate with dilute soda (1 mol.) at the ordinary temperature, and then acidifying the solution; on keeping for a long time, the product is deposited in colourless prisms, and can be recrystallised from boiling water. The yield is 30—40 per cent. of the methyl coumalinate employed. It crystallises with 1 mol. H_2O, which is expelled at 105°, melts at 205—208°, and is readily soluble in alcohol and ether. When methyl coumalinate is kept for some days in contact with water, it is partially transformed into methyl dihydrogen trimesate; free coumalinic acid, on the other hand, seems not to give trimesic acid, even on treatment with alkalis. Trimesic acid melts at about 345—350° (in an air-bath); its ethyl salt crystallises in long, lustrous prisms melting at 133°, and the methyl salt in slender, lustrous needles melting at 144°.

Coumalin,  $\mathrm{CH}{<}\begin{matrix}\mathrm{CH{\cdot}CO}\\ \mathrm{CH{:}CH}\end{matrix}{>}\mathrm{O}$, can be obtained by the dry distillation of mercurous coumalinate in an atmosphere of hydrogen; the yield is about 30 per cent. of the theoretical. It is a colourless oil of sp. gr. 1·20006, 19·5°/4°, but it gradually darkens on exposure to the air; it solidifies on cooling to a mass of crystals which melt at 5°. It boils at 120°, under a pressure of 30 mm. without decomposition, and under the ordinary atmospheric pressure (717 mm.) at 206—209° with slight decomposition; it is miscible with all ordinary solvents, but it separates from its aqueous solution on the addition of potassium carbonate. It is not acted on by boiling water, but it is decomposed by alkalis with formation of crotonaldehyde and carbonic anhydride.

F. S. K.

Orthocyanobenzyl Chloride and Orthocyanobenzal Chloride. By A. Drory (*Ber.*, **24**, 2563—2574).—Gabriel and Day (Abstr., 1890, 1249), by the action of concentrated sulphuric acid on orthocyanobenzyl thiocyanate, have obtained a compound, C_8H_7NS, which behaves both like a mercaptan and like a base. The author has examined the corresponding selenium compounds.

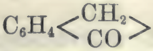
Orthocyanobenzyl selenocyanate, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}SeCN$, is obtained by mixing an alcoholic solution of orthocyanobenzyl chloride with an alcoholic solution of potassium selenocyanate, and heating the mixture in a reflux apparatus for $\frac{1}{4}$—$\frac{1}{2}$ hour. It crystallises from benzene in compact, colourless, rhombohedra or prisms, melts at 121°, completely decomposes at 200°, and is soluble in methyl and ethyl alcohol, ether, petroleum, carbon bisulphide, acetone, and benzene.

Selenophthalimidine (orthocyanobenzyl selenomercaptan), C_8H_7NSe, is obtained by gradually adding orthocyanobenzyl selenocyanate (10 grams) to concentrated sulphuric acid (75 c.c.). Carbonic anhydride is evolved, and a clear solution is obtained. The mixture is poured into iced water, excess of sodium carbonate added, and the resulting emulsion extracted with ether. The product is a yellow oil, has a nauseous odour, partially solidifies on remaining in a closed vessel and melts again at 30°. It is soluble in chloroform, petroleum, benzene, alcohol, and ether, decomposes on exposure to air, yielding orthocyanobenzyl diselenide, and cannot be distilled without decomposition. It dissolves completely in acids, is precipitated from solution by alkalis, and is again dissolved by excess of alkali. The salts of selenophthalimidine crystallise well from alcohol in prismatic needles, and are decomposed on evaporating the aqueous solution on the water-bath. The *hydrochloride* is sparingly soluble in water and alcohol, and is obtained in long, flat, prismatic needles by evaporating an aqueous solution in a vacuum over sulphuric acid. The *platinochloride* is precipitated as an orange-yellow, insoluble, and infusible powder. The *picrate* is obtained as an intensely yellow, crystalline precipitate, is sparingly soluble in alcohol, and decomposes at 170° without melting. The *hydrobromide* crystallises in colourless, prismatic needles, and melts at 264°. The *sulphate* crystallises from water in slender, silky needles, melts at 145—150° with frothing, and, on boiling its aqueous solution, decomposes yielding selenophthalide.

Selenophthalimidine periodide, $C_8H_8NSeI_2$, is obtained by heating orthocyanobenzyl selenocyanate (5 grams) with hydriodic acid (20 c.c.; sp. gr. = 1·70) for five hours at 100°. The product is washed with ether and crystallised from alcohol. It crystallises in slender, dark-violet needles, melts at 223° with decomposition, and is sparingly soluble in boiling alcohol, and almost insoluble in all other solvents.

Orthocyanobenzyl methyl selenide, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}SeMe$, is obtained by the action of methyl iodide (2 grams) on a solution of selenophthalimidine hydrochloride (4 grams) in alcoholic potash. The product is distilled with steam and extracted with ether. It is a yellowish-brown oil, has an unpleasant odour, and distils at 180—200° without decomposition.

Orthocyanobenzyl diselenide, $(CNC_6H_4{\cdot}CH_2)_2Se_2$, is obtained when a solution of a salt of the compound C_8H_7NSe is treated with sodium hydroxide and extracted with ether. It crystallises in needles, melts at 108—110° with decomposition, and is soluble in methyl and ethyl alcohol, benzene, chloroform, and carbon bisulphide.



Selenophthalide, $C_6H_4<{CH_2 \atop CO}>Se$, is obtained on allowing an alcoholic solution of selenophthalimidine to remain with excess of potash in a warm place; ammonia is slowly evolved, and on distilling the mixture in a current of steam an emulsion is obtained which deposits short, nacreous needles of selenophthalide. It crystallises from alcohol in short, colourless leaflets, melts at 58°, and is soluble in alcohol, ether, and benzene.

When orthocyanobenzyl chloride is heated to boiling in a reflux apparatus with copper nitrate and water, the blue colour of the solution remains unaltered; the chloride, however, completely dissolves, and on extracting the solution with ether, phthalide is obtained. Silver nitrate has the same action. Gabriel and Otto, however, obtained phthalide by the action of water alone on orthocyanobenzyl chloride (Abstr., 1887, 1035), and the author points out that as the colour of the above copper solution remains unaltered, the metallic salts are probably without action, and the water alone is necessary.

Orthocyanobenzyl bromide, $CN{\cdot}C_6H_4{\cdot}CH_2Br$, is obtained by leading bromine vapour, by means of a stream of carbonic anhydride, into boiling orthotolunitrile. It is easily soluble in alcohol, ether, benzene, petroleum, &c., sparingly in water, is volatile with steam, melts at 76°, distils without decomposition, and crystallises in the monosymmetric system, $a : b : c = 1{\cdot}5363 : 1 : 0{\cdot}9642$; $\beta = 78° 5'$.

Orthophthalaldehydic acid (m. p. 96°) is obtained when orthocyanobenzal chloride (2 grams) is heated in a reflux apparatus with silver nitrate (4 grams) and water (150 c.c.).

Orthocyanotriphenylmethane is obtained as follows:—Aluminium chloride (7 grams) is gradually added to a mixture of orthocyanobenzal chloride (10 grams), and benzene (40 grams), and the mixture heated on the water-bath as long as hydrogen chloride is evolved. The mixture is then treated with dilute hydrochloric acid, and the layer of benzene which contains the product diluted with ether, separated, dried with calcium chloride, and distilled. After the ether, benzene, and benzal chloride have distilled, an oil is obtained which distils at 270—285° under 20—30 mm. pressure. It is dissolved in absolute alcohol, decolorised with animal charcoal, and allowed to crystallise. It forms slender, white needles, melts at 89°, and is soluble in methyl and ethyl alcohol, ether, chloroform, acetic acid, and benzene, insoluble in petroleum and water. When hydrolysed with 25 per cent. alcoholic potash, it yields *triphenylmethaneorthocarboxylic acid;* this crystallises from acetic acid in slender, white needles, softens at 158°, and melts at 162°.

Orthocyanocinnamic acid, $CN{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COOH$, is obtained by heating cyanobenzal chloride (2 parts) with dry sodium acetate (1 part) and acetic anhydride (10 parts) for 10 hours at 180°. The product is neutralised with sodium carbonate, the unaltered benzal chloride removed by distilling with steam, and the filtered solution precipitated with hydrochloric acid. It crystallises from alcohol in slender, colourless needles, melts at 252°, is soluble in alcohol, ether, acetic acid, chloroform, and benzene, but insoluble in water.

E. C. R.

Preparation of 1 : 2 : 4- and 1 : 3 : 4-Dichlorotoluenes. By H. Erdmann (*Ber.*, **24**, 2769—2771).—1 : 2 : 4-Dichlorotoluene [$Me : Cl_2 = 1 : 2 : 4$] is best prepared from metatolylenediamine by Sandmeyer's method. A solution of 200 grams of cupric chloride in a litre of hydrochloric acid (sp. gr. = 1·175) is boiled with 150 grams of copper turnings until decolorised, then mixed with a solution of 1 kilo. of metatolylenediamine in a litre of hydrochloric acid diluted with a litre of water, and, without cooling, treated with about 9 litres of a 10 per cent. sodium nitrite solution added in a thin stream with constant stirring. The dichlorotoluene, which separates as a heavy, black oil, is steam-distilled, and freed from phenols and azo-derivatives by washing with aqueous soda, drying over solid potash, and afterwards distilling. The yield amounts to 45 per cent. of the theoretical. Pure 1 : 2 : 4-dichlorotoluene boils at 196—197·5° (compare Lellmann and Klotz, Abstr., 1886, 452).

1 : 3 : 4-Dichlorotoluene [$Me : Cl_2 = 1 : 3 : 4$] can be prepared from metachloracetoparatoluidide by converting it into the crude hydrochloride (this vol., p. 1466), and treating this by Sandmeyer's method. The yield of dichlorotoluene from 1 kilo. of paratoluidine by this method was found to be 320 grams.

W. P. W.

Artificial Mineral Lubricating Oil. The Condensation Products of Allyl Alcohol with Methylbenzenes. By G. Kraemer and A. Spilker (*Ber.*, **24**, 2785—2793).—In a previous communication (this vol., p. 206), the authors have described the compounds obtained by the condensation of cinnamene with toluene, xylene, and pseudocumene, and were led to regard them as derivatives of propane. The investigations of Koenigs (this vol., p. 208), and of Liebermann and Hartmann (this vol., p. 1484), however, make it more probable that the compounds in question are ethane derivatives, the methyl radicles in the benzene ring taking no part in the condensation. Xylenecinnamene, previously described as phenyltoluylpropane, must, therefore, be regarded as phenylxylylethane, $CHMePh\cdot C_6H_3Me_2$. At the time the paper on the condensation of cinnamene with xylene was read, the hope was expressed that some light would soon be thrown on the obscure problem of the formation of lubricating oils from petroleum, on account of the resemblance between these oils and cinnamene derivatives, as evidenced not only by the behaviour towards chemical reagents, but also by the fact that cinnamene derivatives containing methyl radicles in the benzene ring exhibit the property of viscosity in a marked degree. For example, phenylxylylethane has a viscosity of 2·1, compared with the value 15 for a medium lubricating oil from Alsatian petroleum, and a value 35 for a good lubricating oil from Caucasian petroleum.

The present paper deals with the condensation of methylbenzenes with allyl alcohol in the presence of sulphuric acid. To bring about the condensation, a mixture of 100 c.c. of pure concentrated sulphuric acid and 50 c.c. of fuming sulphuric acid is gradually added, with vigorous shaking, to a mixture of 100 c.c. of anhydrous allyl alcohol with 1000 c.c. of pseudocumene (xylene, &c.), and precautions are taken against rise of temperature during the reaction. After remaining for some time, the sulphuric acid is carefully separated from the oil, and the latter mixed with a few drops of water to remove the remainder of the acid, and afterwards successively washed with dilute acid, three to four times with water in quantities of 100 c.c., then with 5 per cent. aqueous soda to alkaline reaction, and finally with water until neutral. During the washing, a difficulty arises from the tendency of the two layers to form a stable, white emulsion—a well-known and dreaded occurrence in the manufacture of lubricating oil; this can, however, be overcome by the addition of ether. The oil, after washing, is freed from pseudocumene (xylene, &c.) by a current of steam at 110—120°; the temperature is then raised, and at 200—220° a thick, colourless oil passes over with the steam, leaving a yellowish-brown, resinous substance, which very slowly distils with steam at 250°, and can be purified by fractionally distilling with steam, extracting with ether, &c.

The thick, colourless oil obtained from pseudocumene can be purified by again distilling with steam at about 200°, or better by distillation in a vacuum. It has the composition $C_{21}H_{28}$, giving by Raoult's method numbers which agree well with this formula, and is probably a *dimethyldicumylmethane*. In the pure state it boils above 300° at the ordinary pressure, without appreciable decomposition, and in the viscosimeter gives at 15° the value 775 (water = 1), whilst the best Russian lubricating oil gives the value 40 in the same apparatus. The resinous product of the reaction has the composition $(C_{21}H_{28})_n$, and by Raoult's method gives as a mean of two determinations the value 763 for the molecular weight. The yields from 100 c.c. of allyl alcohol were 122 grams of oil and 90 grams of resin, and from 50 c.c. of alcohol, 52 grams of oil and 50 grams of resin.

The oily product of the condensation of allyl alcohol with xylene has the composition $C_{19}H_{24}$, as confirmed by a determination of the molecular weight by Raoult's method. It is significantly less viscous than the corresponding product (containing two additional methyl radicles) from pseudocumene, and gives the value 8·1 in the same viscosimeter. The yield from 100 c.c. of allyl alcohol amounted to 88 grams of oil and 50 grams of resin.

As a necessary consequence, it would follow that all high boiling fractions of petroleum are free from oxygen, and that the lubricating oils are poorer in hydrogen than the less viscous paraffin oils. These conclusions are borne out by analyses of a commercial lubricating oil of Caucasian origin, and a paraffin oil (viscosity = 15) from Alsatian petroleum. The investigation is being continued, but on account of the difficulty of characterising the products, rapid progress is not to be expected. W. P. W.

Artificial Musk. By A. Baur (*Ber.*, **24**, 2832—2843).—The artificial musk described in a previous communication (Abstr., 1890, 1401) was regarded as trinitroisobutyltoluene. It is, however, a derivative, not of isoprimary but of tertiary butyltoluene, owing to the occurrence in the preparation of the hydrocarbon of an intramolecular change, corresponding with that observed by Schramm in the case of the condensation of benzene with isobutyl bromide by the Friedel-Crafts method (Abstr., 1889, 127).

Tertiary butyltoluene is easily obtained by the action of tertiary butyl chloride on toluene in the presence of aluminium chloride. It boils at 185—187°, and agrees in properties with the so-called isobutyltoluene. The *sulphonic acid*, prepared by warming it with concentrated sulphuric acid, forms a *barium* salt, $(C_{11}H_{15}SO_3)_2Ba + H_2O$, which crystallises in white scales, and dissolves sparingly in cold water, but more easily in hot water, and in 50—60 per cent. alcohol. The *sulphonamide*, $C_{11}H_{15}\cdot SO_2NH_2$, crystallises from water in nacreous scales, and melts at 94—95°. Earlier determinations with the sulphonamide prepared from so-called isobutyltoluene gave 74—75° as the melting point, and this value is always obtained with the freshly-prepared substance; after being kept for some hours, the melting point is found to have risen to and remains constant at 94—95°. The trinitrobutyltoluene formed by the nitration of tertiary butyltoluene melts at 96—97°, and is identical with the product from so-called isobutyltoluene.

Nitrobutyltoluene, $CMe_3\cdot C_6H_3Me\cdot NO_2$, is obtained by slowly adding fuming nitric acid to a solution of tertiary butyltoluene in acetic acid. It is a yellowish oil of a peculiar and slightly unpleasant odour, boils at 160—162° in a vacuum without decomposition, and is readily volatile with steam. On treatment with excess of nitric acid, it is converted into artificial musk.

Dinitrobutyltoluene, $CMe_3\cdot C_6H_2Me(NO_2)_2$, is formed, together with the mononitro- and trinitro-derivatives when tertiary butyltoluene is dissolved in well-cooled nitric acid of sp. gr. 1·5. On distillation with steam, the mononitro-derivative passes over first, and then a mixture of the mononitro- and dinitro-derivatives distils over, leaving a residue of the trinitro-derivative mixed with a very small quantity of the dinitro-compound. A separation of the dinitrobutyltoluene can be more easily effected by crystallising out the greater part of the trinitrobutyltoluene, repeatedly distilling the oil in a vacuum, and collecting the fraction boiling at 224—225°. Dinitrobutyltoluene is a brown oil of very unpleasant odour, and does not solidify in a freezing mixture. On further nitration, it is converted into artificial musk.

Trinitrobutyltoluene (artificial musk), $CMe_3 \cdot C_6HMe(NO_2)_3$, is obtained when tertiary butyltoluene is slowly added in the cold to five times its weight of a mixture of 1 part of nitric acid (sp. gr. = 1·5) and 2 parts of 15 per cent. anhydrosulphuric acid, and the mixture afterwards heated for 8—9 hours on a water-bath. It crystallises from alcohol in yellowish-white needles, melts at 96—97°, is only very slightly volatile with steam, and has a powerful odour of musk. It is insoluble in water, but it dissolves readily in alcohol, ether, benzene, chloroform, and light petroleum. With naphthalene in alcoholic solution, it forms a compound $2C_{11}H_{13}(NO_2)_3,C_{10}H_8$, which crystallises in large, yellowish scales, melts at 89—90°, and decomposes into its generators on warming with water. Trinitrobutyltoluene is not affected by treatment with alkalis or ammonia, and when warmed with an excess of aniline forms a compound $3C_{11}H_{13}(NO_2)_3,2NH_2Ph$, which crystallises from the excess of aniline in compact forms, and melts at 64°. Of the four possible formulæ for a trinitrometabutyltoluene, the author, on these grounds, excludes the three containing two nitro-radicles relatively in the ortho-position, and assigns to artificial musk the remaining formula

$$[Me : CMe_3 : (NO_2)_3 = 1 : 3 : 2 : 4 : 6].$$

Amidobutyltoluene, $CMe_3 \cdot C_6H_3Me \cdot NH_2$, is formed by the reduction of nitrobutyltoluene with tin and hydrochloric acid. It is a colourless oil, of pleasant, cumin-like odour, and boils at 245°. The acetyl derivative, $C_{11}H_{15} \cdot NHAc$, crystallises from alcohol in lustrous scales melting at 162°, and the benzoyl derivative in small, white needles melting at 167—168°. It is therefore identical with the amido-compound obtained by Effront (Abstr., 1884, 899; 1885, 152) by heating isobutyl alcohol with orthotoluidine hydrochloride at 280—300°, and must contain the amidogen in the para-position relatively to the tertiary butyl radicle.

Amidodinitrobutyltoluene, $CMe_3 \cdot C_6HMe(NO_2)_2 \cdot NH_2$, is obtained when trinitrobutyltoluene in alcoholic solution is reduced with the theoretical quantity of ammonium sulphide. It crystallises from alcohol in brownish-yellow needles, melts at 125—126°, and is insoluble in water. The *hydrochloride* crystallises in brown scales, and on treatment in alcoholic solution with ethyl nitrite, gives a *dinitrobutyltoluene*, which could not be crystallised.

Tertiary butylmetaxylene, $C_6H_3Me_2 \cdot CMe_3$ $[Me_2 : CMe_3 = 1 : 3 : 5]$, can be prepared by boiling metaxylene either with isobutyl bromide or tertiary butyl bromide in the presence of aluminium chloride. It is a colourless liquid which boils at 200—202° under 747 mm. pressure, and on oxidation with nitric acid, yields mesitylenic acid, and with chromic acid, trimesic acid. The *trinitro*-derivative, $CMe_3 \cdot C_6Me_2(NO_2)_3$, crystallises from alcohol in yellowish-white needles, melts at 110°, and has a strong, musk-like odour; the *nitro*-derivative, $CMe_3 \cdot C_6H_2Me_2 \cdot NO_2$, formed by adding fuming nitric acid to a cold acetic acid solution of the hydrocarbon, crystallises from alcohol in white needles which melt at 85°, and have a cinnamon-like odour.

Butylethylbenzene, $C_6H_4Et\cdot CMe_3$, is formed by the condensation of ethylbenzene and isobutyl bromide in the presence of aluminium chloride, and is separated from the butyltoluene and butylbenzene produced in the reaction by fractional distillation at 200—205°. It resembles butyltoluene in properties, and yields a *trinitro*-derivative, $CMe_3\cdot C_6HEt(NO_2)_3$, which is more soluble in alcohol than artificial musk, and has a strong, musk-like odour.

Among the secondary products of the reaction between pure toluene and pure isobutyl bromide in the presence of aluminium chloride, are butylbenzene, butylxylene, butylethylbenzene, dibutylbenzene, and dibutyltoluene, and these substances are present in the fraction 170—200°, which was formerly used instead of pure tertiary butyltoluene in the preparation of artificial musk. W. P. W.

Action of Chlorine on Acetoparatoluidide. Preparation of Metachloroparatoluidine. By H. Erdmann (*Ber.*, **24**, 2766—2769).—Hitherto metachloracetoparatoluidide has been prepared by the action of chlorine on acetoparatoluidide, either suspended in water (Wroblewsky, *Annalen*, **168**, 196), or in dilute aqueous solution at 0° (Lellmann and Klotz, Abstr., 1886, 452), and in both cases the yield was small and unsatisfactory. It can, however, be obtained in considerable quantity by dissolving acetoparatoluidide (100 grams) in hot acetic acid (100 c.c.), and passing a rapid stream of chlorine (160 grams) through the solution, which soon becomes boiling hot. To prevent loss of chlorine, three flasks placed in series, and containing the quantities given, are connected with the chlorine generator. The metachloracetoparatoluidide can be easily freed from accompanying resinous matters, and crystallises from alcohol, or from a mixture of chloroform and light petroleum, in needles melting at 111—112°.

Metachloroparatoluidine may be prepared directly from the chlorination product by distilling off the acetic acid, boiling the residue with 20 per cent. hydrochloric acid in a reflux apparatus for 3—4 hours, and afterwards distilling with steam to remove the small quantity of chlorinated cresol formed in the reaction. On cooling, the sparingly soluble hydrochloride separates as a crystalline mass, whilst the more soluble paratoluidine hydrochloride remains in the mother liquor. The crystalline hydrochloride is then decomposed with aqueous soda, and the base freed from the less volatile dichlorotoluidine by steam distillation. The yield, under these conditions, amounts to more than 400 grams from 1 kilo. of commercial paratoluidine, and the product is very fairly pure, boiling at 218—225°. Metachloroparatoluidine, purified by conversion into its sparingly soluble crystalline nitrate, is a colourless oil which boils at 223—224° (corr.), and crystallises in a freezing mixture in lustrous, snow-white scales melting at 7°; on exposure to air and light, it soon becomes coloured. W. P. W.

γ-Phenoxypropylamine. By J. LOHMANN (*Ber.*, **24**, 2631—2641). —*γ-Bromopropyl phenyl ether*, $CH_2Br\cdot CH_2\cdot CH_2\cdot OPh$, is formed, together with a small proportion of trimethylene diphenyl ether, when an alcoholic solution of trimethylene bromide (41 grams) and sodium phenoxide (15 grams) is heated in a reflux apparatus for about four hours on a water-bath. After removal of the alcohol by distillation, the product is steam-distilled, and the distillate extracted with ether; the residue left after evaporation of the ether is freed from phenol by extraction with dilute aqueous soda, and from trimethylene bromide by fractional distillation. The yield amounts to about 40 per cent. of the theoretical. The ether is an oil which boils at 246—256° with decomposition, and dissolves in most solvents except water.

γ-Phenoxypropylphthalimide, $C_8H_4O_2{:}N\cdot C_3H_6\cdot OPh$, is obtained by heating equal weights of γ-bromopropyl phenyl ether and potassium phthalimide at 220° for an hour. It crystallises from alcohol in white needles, melts at 88°, and is easily soluble in most solvents. When heated with concentrated hydrochloric acid at 180—185° for 4—5 hours, it is decomposed into a mixture of phthalic acid, phenol, and γ-chloropropylamine hydrochloride.

γ-Phenoxypropylphthalamic acid, $OPh\cdot C_3H_6\cdot NH\cdot CO\cdot C_6H_4\cdot COOH$, is obtained by boiling γ-phenoxypropylphthalimide with dilute aqueous potash until dissolved, pouring the solution into cold water, and acidifying with hydrochloric acid. It is a white, crystalline powder which melts at 134°, is insoluble in almost all solvents except alcohol, and regenerates the imide on boiling with alcohol. When heated with 5—6 times its weight of hydrochloric acid in a reflux apparatus for about an hour, it decomposes into phthalic acid and γ-phenoxypropylamine hydrochloride. *γ-Phenoxypropylamine*, $OPh\cdot C_3H_6\cdot NH_2$, is a colourless oil which boils at 241—242° under 766 mm. pressure, and readily absorbs carbonic anhydride from the air. The *hydrochloride*, $C_9H_{13}NO,HCl$, crystallises from alcohol in lustrous, pale-yellow scales, and melts at 168°; the *picrate* and *platinochloride*, $(C_9H_{13}NO)_2,H_2PtCl_6$, are crystalline. The *benzoyl* derivative,

$$OPh\cdot C_3H_6\cdot NHBz,$$

crystallises from alcohol in white needles melting at 118°, and the *carbamide*, $OPh\cdot C_3H_6\cdot NH\cdot CONH_2$, in silvery scales melting at 114°.

γ-Diphenoxypropylamine, $(OPh\cdot C_3H_6)_2NH$, is formed, together with a small quantity of γ-phenoxypropylamine when γ-bromopropyl phenyl ether (12 grams) is digested with 10 per cent. alcoholic ammonia (15—20 c.c.) at 100° for 2—3 hours. It is an oil boiling at above 300°. The *hydrochloride*, $C_{18}H_{23}NO_2,HCl$, crystallises from alcohol in transparent needles, melts at 206°, and is very sparingly soluble in water. The *nitrosamine*, $C_{18}H_{24}O_2N\cdot NO$, crystallises from alcohol in pale-yellow, lustrous scales, melts at 60—61°, dissolves readily in most solvents except water, and decomposes into γ-diphenoxypropylamine and ammonia on reduction in alcoholic solution with zinc-dust.

γ-Phenoxypropylaniline, $OPh\cdot C_3H_6\cdot NHPh$, is prepared by heating γ-bromopropyl phenyl ether (12 grams) with aniline (15 grams) for about two hours on a water-bath, and subsequently removing the excess of aniline by steam distillation. It is a brown oil of basic odour, and boils at above 300°, dissolves in most solvents with the exception of water, and on standing solidifies to a mass which melts at 32°. The *hydrochloride*, $C_{15}H_{17}NO,HCl$, crystallises from alcohol in needles, melts at 170°, and, when warmed with water, is partly dissolved and partly decomposed into the base and hydrochloric acid.

γ-Phenoxybutyronitrile, $OPh{\cdot}C_3H_6{\cdot}CN$, is obtained when γ-bromopropyl phenyl ether (20 grams), alcohol (180 c.c.), and a solution of potassium cyanide (18 grams) in water (36 c.c.) are heated together for 3—4 hours in a reflux apparatus. It crystallises in white needles, melts at 45—46°, boils at 287—289°, and dissolves easily in the ordinary solvents. On hydrolysis with concentrated hydrochloric acid at 100°, it is converted into *γ-phenoxybutyric acid*, $OPh{\cdot}C_3H_6{\cdot}COOH$, which crystallises from light petroleum in silvery scales, melts at 60°, and is insoluble in water, sparingly soluble in hydrochloric acid, light petroleum, and carbon bisulphide, and easily soluble in alcohol, ether, chloroform, and benzene. When dissolved in 5—6 times its weight of cold concentrated sulphuric acid, and left for 5—6 hours, the nitrile undergoes both hydrolysis and sulphonation with the production of *sulpho-γ-phenoxybutyramide*, $SO_3H{\cdot}C_6H_4{\cdot}O{\cdot}C_3H_6{\cdot}CONH_2$. This substance melts at 211°, can be crystallised from water, is insoluble in alcohol, benzene, chloroform, &c., and yields salts on treatment with carbonates.

Trimethylene diphenyl ether, $OPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OPh$, formed as a secondary product in the preparation of γ-bromopropyl phenyl ether, crystallises from alcohol in lustrous scales, melts at 61°, does not volatilise with steam, and is readily soluble in most solvents.

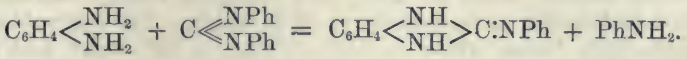
γ-Phenoxypropyl alcohol, $OPh{\cdot}C_2H_4{\cdot}CH_2{\cdot}OH$, prepared by treating a hot aqueous solution of γ-phenoxypropylamine hydrochloride with a hot solution of sodium nitrite, is an oily liquid boiling at 240—250° under 764 mm. pressure.

Trimethylene phenyl methyl ether, $OPh{\cdot}C_3H_6{\cdot}OMe$, is obtained when γ-bromopropyl phenyl ether is boiled with the calculated quantity of sodium methoxide in methyl alcohol solution for 2—3 hours in a reflux apparatus. It is an oily liquid boiling at 230—231°.

Trimethylene phenyl ethyl ether, $OPh{\cdot}C_3H_6{\cdot}OEt$, formed by boiling γ-bromopropyl phenyl ether with alcoholic potash for two hours in a reflux apparatus, is a colourless, oily liquid of pleasant odour, and boils at 328—330° under 760 mm. pressure. W. P. W.

Products of the Action of Aromatic Carbodiimides on Orthodiamines. By A. Keller (*Ber.*, **24**, 2498—2525).—According to the investigations of Dahm and Gasiorowski (Abstr., 1887, 247), and of Moore (Abstr., 1889, 983; 1890, 246), orthodiamines combine with carbodiphenylimide and carbodiparatolylimide in molecular proportions. The author in continuing Moore's experiments has obtained results differing considerably from those of the latter investigator, and has therefore repeated the whole of the work with the following results :—

Carbodiphenylimide and orthophenylenediamine were heated together in molecular proportion for five minutes at 210—220°, and the product, which smells strongly of aniline, distilled in a current of steam. The distillate contains aniline in considerable quantity, whilst the residue, after recrystallisation from benzene or alcohol, forms white needles or prisms, and melts at 190°. It has the composition $C_{13}H_{11}N_3$, and appears to be *phenylorthophenyleneguanidine*, its formation being represented as follows :—



$$C_6H_4{<}\substack{NH_2\\NH_2} + C{\lll}\substack{NPh\\NPh} = C_6H_4{<}\substack{NH\\NH}{>}C{:}NPh + PhNH_2.$$

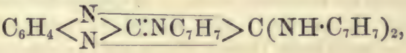
It crystallises from alcohol, when the solution is allowed to evaporate slowly, in thick, apparently monosymmetric prisms, is almost insoluble in water and light petroleum, sparingly soluble in ether, and readily in alcohol. It distils with slight decomposition at 440—450°, but may be volatilised unchanged under 30 mm. pressure, and has then a vapour density corresponding with the above formula. It is a very stable substance, and is only attacked by hydrochloric acid at 300°. The *hydrochloride*, $C_{13}H_{11}N_3,HCl$, forms long, white, hair-like needles, and is soluble in water and alcohol; the *platinochloride*, $(C_{13}H_{11}N_3)_2,H_2PtCl_6$, is a pale-yellow, crystalline powder, almost insoluble in water; the *sulphate*, $(C_{13}H_{11}N_3)_2,H_2SO_4$, crystallises in long, hair-like needles, and is slightly soluble in cold, readily in hot water and in alcohol; the *acetyl* compound, $C_{13}H_{10}N_3Ac$, is unstable, and crystallises from benzene in fascicular aggregates of prisms melting at 160°; and the *dibenzoyl* compound, $C_{13}H_9N_3Bz_2$, crystallises in fascicular aggregates of white, lustrous needles, and melts at 171°. If the base is dissolved in acetic acid and mixed with an aqueous solution of potassium nitrite, a pale-yellow, crystalline precipitate of the *nitroso*-compound $C_{13}H_{10}N_3{\cdot}NO$ is formed, which separates from all solvents as an oil, and shows Liebermann's reaction.

As the phenylorthophenyleneguanidine contains two imido-groups, it appeared probable that it would combine with phenyl isocyanate forming a double carbamide. This reaction does in all probability take place, but the product at once loses aniline, forming the compound $C_6H_4{<}\substack{N\\N}\overline{\underline{>C{:}NPh}}\substack{CO\\CO}{>}NPh$, which crystallises from alcohol in thin, lustrous, white needles, melts at 264—266°, is insoluble in water and light petroleum, but soluble in alcohol and benzene.

According to Moore (*loc. cit.*), 2 mols. of carbodiphenylimide also unite directly with 1 mol. of orthophenylenediamine, forming the compound $C_6H_4N_2[C(NHPh)_2]_2$; the author finds, however, that the products of the reaction are aniline, phenylorthophenyleneguanidine, and triphenylguanidine (m. p. 144°). If, on the other hand, phenylorthophenyleneguanidine is treated with a second molecule of carbodiphenylimide at 210°, the compound *diphenylamidomethylenephenylorthophenyleneguanidine*, $C_6H_4{<}\substack{N\\N}\overline{\underline{>C{:}NPh}}{>}C(NHPh)_2$, is formed, which crystallises from alcohol in white needles and melts at 188°; the yield is small, owing to the secondary reactions which take place. If carbodiparatolylimide is substituted for carbodiphenylimide, the corresponding *paratolyl* derivative is obtained; it crystallises in white needles and melts at 185—187°.

Paratolylorthophenyleneguanidine, $C_6H_4{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C\colon N\cdot C_7H_7$, is obtained on heating together orthophenylenediamine and carbodiparatolylimide; it crystallises from alcohol in short, thick, slightly brownish tablets, melts at 209°, and dissolves readily in boiling alcohol and acetic acid, scarcely at all in water. The *hydrochloride*, $C_{14}H_{13}N_3,HCl$, forms white needles, soluble in hot water and cold alcohol; the *platinochloride*, $(C_{14}H_{13}N_3)_2,H_2PtCl_6$, is a pale-yellow, microcrystalline precipitate; the *sulphate*, $(C_{14}H_{13}N_3)_2,H_2SO_4$, crystallises in long, white needles; the *acetyl* compound, $C_{14}H_{12}N_3Ac$, forms unstable, white needles and melts at 152°; and the *dibenzoyl* compound, $C_{14}H_{11}N_3Bz_2$, crystallises in long, lustrous prisms, melting at 191°. The *nitroso*-compound, $C_{14}H_{12}N_3\cdot NO$, forms yellow, crystalline flakes, and commences to decompose at 90°.

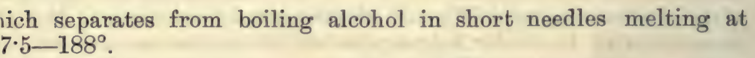
Paratolylorthophenyleneguanidine combines with phenyl isocyanate, forming the compound $C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}\overline{\underline{C\colon NC_7H_7}}\genfrac{}{}{0pt}{}{CO}{CO}{>}NPh$, which crystallises in small needles and melts at 252—254°. With carbodiparatolylimide, the base yields the compound



$$C_6H_4{<}\genfrac{}{}{0pt}{}{N}{N}{>}\overline{\underline{C\colon NC_7H_7}}{>}C(NH\cdot C_7H_7)_2,$$

which separates from boiling alcohol in short needles melting at 187·5—188°.

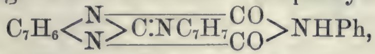
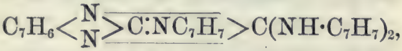
Phenylorthotoluyleneguanidine, $C_7H_6{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C\colon NPh$, is obtained together with aniline by heating orthotoluylenediamine with carbodiphenylimide in molecular proportion. It crystallises from alcohol in short, white needles, and from benzene in prisms, and melts at 166—167°; the *hydrochloride*, $C_{14}H_{13}N_3,HCl$, forms long, white, elastic, silky needles; the *platinochloride*, $(C_{14}H_{13}N_3)_2,H_2PtCl_6 + 3H_2O$, large, orange-yellow tablets; the *sulphate*, $(C_{14}H_{13}N_3)_2,H_2SO_4$, long, white, lustrous needles; the *acetyl* compound, $C_{14}H_{12}N_3Ac$, white needles, melting at 144—147°; the *dibenzoyl* compound fascicular aggregates of prisms, melting at 220—222°; the *nitroso*-compound, $C_{14}H_{12}N_3\cdot NO$, is a flocculent precipitate, melting at 120—125° with decomposition. The base combines with phenyl isocyanate and carbodiphenylimide to form the compounds



$$C_7H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}\overline{\underline{C\colon NPh}}\genfrac{}{}{0pt}{}{CO}{CO}{>}NPh \text{ and } C_7H_6{<}\genfrac{}{}{0pt}{}{N}{N}{>}\overline{\underline{C\colon NPh}}{>}C(NHPh)_2,$$

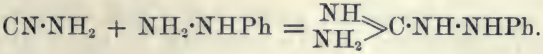
melting at 230—234° and 199—200° respectively. The *diparatolyl* compound corresponding with the latter melts at 190—193°.

Paratolylorthotoluyleneguanidine, $C_7H_6{<}\genfrac{}{}{0pt}{}{NH}{NH}{>}C\colon N\cdot C_7H_7$, is obtained by heating together orthotoluylenediamine and carbodiparatolylimide; it crystallises from alcohol in white prisms, and melts at 197—198°. The *hydrochloride*, $C_{15}H_{15}N_3,HCl$, forms long, white, silky needles; the *platinochloride*, $(C_{15}H_{15}N_3)_2,H_2PtCl_6$, orange-coloured tablets; the *sulphate*, $(C_{15}H_{15}N_3)_2,H_2SO_4 + 5H_2O$, lustrous, white needles; the *acetyl* compound, $C_{15}H_{14}N_3Ac$, long, white needles melting at 148—149°; the *dibenzoyl* compound, $C_{15}H_{13}N_3Bz_2$, fascicular aggregates of white needles melting at 198—201°; the *nitroso*-compound, $C_{15}H_{14}N_3\cdot NO$, commences to decompose at 130°.

Tolyltoluyleneguanidine combines with phenyl isocyanate, yielding the compound  $C_7H_6<{N \atop N}\!>\overline{C{:}NC_7H_7}{CO \atop CO}\!>NHPh$, which crystallises from alcohol in small needles, and melts at 230—233°. With carbodiparatolylimide, it forms  $C_7H_6<{N \atop N}\!>\overline{C{:}NC_7H_7}>C(NH\cdot C_7H_7)_2$, which melts at 208—210°; the corresponding *diphenyl* compound melts at 174—176°.

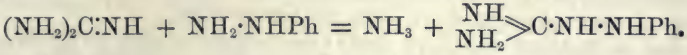
H. G. C.

Anilguanidine. By G. PELLIZZARI (*Gazzetta*, **21**, 330—340).—Cyanamide reacts with phenylhydrazine hydrochloride to form anilguanidine hydrochloride,



$$CN\cdot NH_2 + NH_2\cdot NHPh = {NH \atop NH_2}\!\!>C\cdot NH\cdot NHPh.$$

The same product is obtained by the action of phenylhydrazine on guanidine,

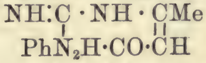


$$(NH_2)_2C{:}NH + NH_2\cdot NHPh = NH_3 + {NH \atop NH_2}\!\!>C\cdot NH\cdot NHPh.$$

Anilguanidine hydrochloride, $C_7H_{10}N_4,HCl$, is obtained by boiling a solution of cyanamide (18 grams) and phenylhydrazine hydrochloride (60 grams) in alcohol (300 grams) for 12 hours; the greater part of the alcohol is then evaporated, very dilute hydrochloric acid added, and the solution allowed to cool after expulsion of the remaining alcohol. The salt separates in reddish crystals, which, on recrystallisation from water, form yellowish, acicular crystals, very soluble in hot alcohol and water, less so in hydrochloric acid. It melts with decomposition at 226°, and reduces ammoniacal silver nitrate solution. A yield of 50 per cent. is obtained by the above method; the mother liquors contain another base not yet studied. The hydrochloride may also be obtained by gradually heating guanidine carbonate with phenylhydrazine hydrochloride to 180°, the crude product being crystallised from dilute hydrochloric acid. The yield is, however, a poor one. *Anilguanidine platinochloride*, $(C_7H_{10}N_4)_2,H_2PtCl$, is precipitated in minute, yellowish, prismatic crystals frequently twined crosswise. It is soluble in hot water, but after a time is reduced with separation of metallic platinum. The *carbonate*, $(C_7H_{10}N_4)_2,H_2CO_3 + H_2O$, forms minute, white scales, which are slowly coloured red on exposure to the air. On heating, it loses ammonia and water, yielding a new base not yet investigated. The *acetate*, $C_7H_{10}N_4,C_2H_4O_2$, is obtained in small, colourless crystals which decompose at 195°; it is very soluble in alcohol.

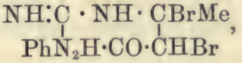
When concentrated potash is added to the solution of the hydrochloride, the free base separates in little drops, which soon solidify to yellow, needle-shaped crystals. It changes spontaneously in air, and is obtained pure only with great difficulty.

Ethyl acetoacetate reacts with anilguanidine, forming a closed chain compound. A solution of anilguanidine hydrochloride (10 grams), ethyl acetoacetate (7 grams), and sodium carbonate (2·8 grams) in alcohol (50 c.c.) is boiled for seven hours, the alcoholic solution partly evaporated, dissolved in water, and acidified with acetic acid; on cooling, the new compound (8 grams) is obtained. By recrystallisation from alcohol, it may be obtained in white crystals of the composition $C_{11}H_{12}N_4O$, which on heating turn red and slowly decompose without melting. The reaction may be represented by the equation $C_6H_{10}O_3 + C_7H_{10}N_4 = H_2O + C_2H_6O + C_{11}H_{12}N_4O$; the product is probably



$\begin{array}{l} NH{:}C\cdot NH\cdot CMe \\ PhN_2H\cdot CO\cdot CH \end{array}$

. The *dibromo-derivative*,



$$\begin{array}{l} NH{:}C\cdot NH\cdot CBrMe \\ PhN_2H\cdot CO\cdot CHBr \end{array},$$

is obtained on bromination in glacial acetic acid solution, and consists of minute, colourless crystals, insoluble in water and alcohol, slightly soluble in acetic acid, and decomposing at 220—222°.

The *ethyl derivative*, $C_{13}H_{16}N_4O$, is obtained on treating anilguanidine hydrochloride with ethyl ethylacetoacetate in alcoholic solution, as spherical aggregates of short, thin, yellow prisms.

When a mixture of ethyl diethylacetoacetate and anilguanidine hydrochloride is treated as above, no reaction occurs even when the heating is continued for some days. W. J. P.

Halogenated Amines of the Fatty Series. By O. SEITZ (*Ber.*, **24**, 2624—2631).—With the object of preparing chlorinated amines of the fatty series, the author has treated potassium phthalimide with various chlorobromides by Gabriel's method (Abstr., 1888, 439) in the hope that the more reactive bromine would alone be eliminated with the production of chlorethyl- or chloropropylphthalimide. Trimethylene chlorobromide, however, yields a mixture of γ-chloropropyl- and γ-bromopropyl-phthalimide, and ethylene chlorobromide in like manner gives a mixture of chlorethyl- and bromethyl-phthalimide.

Chlorethylphthalimide, $C_8H_4O_2{:}N\cdot CH_2\cdot CH_2Cl$, is obtained when potassium phthalimide is heated with five times its weight of ethylene dichloride at 180—190° for three hours. It crystallises from carbon bisulphide in colourless needles, melts at 79—81°, and, when heated with concentrated hydrochloric acid at 180° for four hours, yields phthalic acid and chlorethylamine hydrochloride. The latter can be crystallised from amyl alcohol, in which it is less soluble than in the ordinary solvents, and melts at 119—123°; the picrate and platinochloride of the amine have already been described (*loc. cit.*).

β-Bromopropylphthalimide, $C_8H_4O_2{:}N\cdot CH_2\cdot CHBrMe$, is formed when a mixture of allylphthalimide (1·5 grams) with concentrated hydrobromic acid prepared at 0° (6 c.c.) is allowed to remain in a stoppered flask for 24 hours at the ordinary temperature. It separates from methyl alcohol as a silky, felted, crystalline mass, and melts at 105°.

β-Thiocyanopropylphthalimide, $C_8H_4O_2\colon N\cdot CH_2\cdot CHMe\cdot SCN$, is prepared by heating β-bromopropylphthalimide with alcoholic potassium thiocyanate at 170° for four hours. It dissolves in methyl alcohol, cold benzene, and acetic acid, but less readily in light petroleum, and melts at 89—93°.

β-Mercaptopropylphthalimide, $C_8H_4O_2\colon N\cdot CH_2\cdot CHMe\cdot SH$, is obtained when β-bromopropylphthalimide is heated with alcoholic potassium hydrosulphide in a pressure flask for one hour at 100°. After purification by conversion into its mercury salt, it crystallises from alcohol in aggregates melting at 88°. When oxidised by the addition of iodine to its alcoholic solution, it is converted into *β-diphthalimidopropyl bisulphide*, $(C_8H_4O_2\colon N\cdot CH_2\cdot CHMe)_2S_2$, which crystallises in white needles and melts at 159—161°.

The action of aniline on β-bromopropylphthalimide is essentially different from that on the γ-compound (compare Goldenring, Abstr., 1890, 976), and is by no means complete at 150°. When aniline (8 grams) and β-bromopropylphthalimide (9 grams) are heated together on a sand-bath for 20 minutes, a mixture of phthalanil, as chief product, with a relatively small proportion of *β-anilidopropylphthalimide*, $C_8H_4O_2\colon N\cdot CH_2\cdot CHMe\cdot NHPh$, is obtained. The latter crystallises from alcohol in beautiful yellow needles, melts at 93°, and on digestion with concentrated hydrochloric acid at 190°, is decomposed into phthalic acid and a base, probably β-anilidopropylenediamine, $NHPh\cdot CH(CH_2\cdot NH_2)_2$, boiling at 250—260°.

W. P. W.

Azoimide. By E. Noelting and E. Grandmougin (*Ber.*, **24**, 2546—2547).—Curtius has shown (this vol., p. 56) that triazobenzene or diazobenzeneimide must be regarded as the phenyl salt of azoimide. In view of the stability of such aromatic salts, there appeared little likelihood of eliminating the phenyl group, but it seemed not improbable that the entrance of nitro-groups into the phenyl residue might render the elimination more easy, just as is the case with chlorobenzene.

An experiment with dinitrotriazobenzene has shown that such is really the case. The dinitro-compound was prepared from 1 : 2 : 4-dinitraniline by diazotising, converting into the perbromide, and treating this with ammonia; by the action of alcoholic potash, it is converted, apparently very readily, into dinitrophenol and azoimide.

H. G. C.

Orthohydroxyazo-dyes. By J. D. Zibell (*Chem. Centr.*, 1891, ii, 56; from *Schweiz. Wochenschr. Pharm.*, **29**, 186; compare Abstr., 1884, 742 and 1146).—The author finds that diazobenzene chloride reacts with parahydroxybenzoic acid with separation of the carboxyl group, forming phenylazophenol and phenyldiazophenol. Diazosulphanilic acid reacts similarly, forming sodium phenolazosulphanilate. On the other hand, the azo-compounds obtained by employing ortho- and meta-hydroxybenzoic acids behaved differently from one another when cotton was dyed with them, only that obtained from orthohydroxybenzoic acid adhering to the fibre. J. W. L.

Thiocarbamides. By H. SALKOWSKI (*Ber.*, **24**, 2724—2729).—Symmetrical dibenzylthiocarbamide, $CS(NH·CH_2Ph)_2$, may be readily obtained by heating benzylamine benzylthiocarbamate at 125° until hydrogen sulphide ceases to be evolved; it melts at 148°, not at 114° as stated by Strakosch.

Benzylthiocarbamide, $NH_2·CS·NH·CH_2Ph$, is prepared by heating benzylamine thiocyanate at 110° for about 14 hours, and is identical with the product formed by the action of alcoholic ammonia on benzylthiocarbimide; it is soluble in 61 parts of 95 per cent. alcohol, crystallises in colourless, concentric needles, and melts at 164°. Paternò and Spica give the melting point as 101°, and state that the compound is readily soluble in water; they appear, however, to have mistaken benzylamine thiocyanate for benzylthiocarbamide, since the latter is almost insoluble in water, and the former melts, according to the author, at 95°.

Paternò and Spica have made a similar error regarding unsymmetrical dibenzylthiocarbamide, $NH_2·CS·N(CH_2Ph)_2$, which they obtained by the evaporation of benzylamine hydrochloride and potassium thiocyanate solutions; the author failed to detect the formation of any thiocarbamide in this manner. *Dibenzylamine thiocyanate* is prepared by dissolving dibenzylamine in hot dilute thiocyanic acid; it crystallises in colourless, lustrous plates melting at 164—165°. On melting the compound and heating it at 140° for several hours, unsymmetrical dibenzylthiocarbamide is formed; this is insoluble in water, and is deposited from alcohol in small, yellow crystals which melt at 141°.

Contrary to the statement of Clermont, aniline thiocyanate is readily converted into phenylthiocarbamide by dissolving the salt in water, evaporating to dryness, and heating the residue for 2—3 hours on the water-bath. The conversion of methylamine thiocyanate into the corresponding thiocarbamide has not as yet been observed by the author.

Methylthiocarbamide, prepared from methylthiocarbimide and alcoholic ammonia, melts at 119—120° instead of below 100° as usually stated in text books.

The observations of O. Hecht regarding symmetrical dimethylthiocarbamide are confirmed.

The above results prove that, in certain cases at all events, the conversion of amine thiocyanates into the corresponding thiocarbamides is independent of the former compounds being in the nascent state. J. B. T.

Derivatives of Bromopiperonal. By A. OELKER (*Ber.*, **24**, 2592—2596).—Bromopiperonal, $CH_2O_2⁚C_6H_2Br·COH$, is obtained by adding the calculated quantity of bromine to a solution of piperonal in carbon bisulphide in the presence of a small quantity of iodine. The carbon bisulphide is distilled off and the mass boiled with alcohol.

On cooling, it separates in long, white needles, melts at 129—130°, and is identical with the compound obtained by Fittig and Mielk (*Annalen*, **152**, 39).

Bromopiperonalphenylhydrazone is obtained in yellow, nacreous scales on adding phenylhydrazine to a solution of the above compound in dilute acetic acid. It melts at 136°, is insoluble in water, and easily soluble in alcohol, ether, and acetone.

Bromopiperonaldoxime is obtained by adding an aqueous solution of hydroxylamine hydrochloride to an alcoholic solution of bromopiperonal. It forms slender, white needles, crystallises from alcohol, melts at 168°, is insoluble in water, but easily soluble in alcohol, ether, and benzene.

Mononitrobromopiperonal, $CH_2O_2{:}C_6HBr(NO_2)\cdot COH$, is obtained by adding twice the theoretical quantity of nitric acid (1·48) to a cold solution of bromopiperonal in acetic acid. Heat is developed, and the solution must be cooled below 50°, otherwise the action becomes too violent, and the bromopiperonal is decomposed. The mixture is poured into ice-cold water, and the product crystallised from alcohol. It crystallises in beautiful, bright-yellow needles, melts at 90°, and is soluble in all the ordinary solvents except water. When treated with acetone and caustic soda, the mixture becomes red, and an indigo-compound is not formed; hence the author is inclined to believe that the nitro-group is in the meta-position with respect to the aldehyde group. However, dinitrobromopiperonal, in which one nitro-group must be in the ortho-position relatively to the aldehyde group, behaves in a similar way, and does not yield an indigo compound with acetone and alkali. The red coloration is also produced by boiling the compound with alkalis alone, and disappears on the addition of hydrochloric acid.

Dinitrobromopiperonal is obtained by adding bromopiperonal in small portions to well-cooled nitric acid (sp. gr. 1·52), and pouring the solution into ice-cold water. It crystallises from alcohol and acetone in golden-yellow needles, melts at 173°, is insoluble in water, somewhat sparingly soluble in alcohol and ether, easily so in acetone and chloroform, and turns deep yellow on exposure to light.

Bromopiperonylacryl methyl ketone, $CH_2O_2{:}C_6H_2Br\cdot CH{:}CH\cdot COMe$, is formed, together with dibromodipiperonylacryl methyl ketone, by shaking bromopiperonal (5 grams) with acetone (15 c.c.) and 3 per cent. caustic soda (4—5 c.c.). It is separated by extracting the product with a small quantity of alcohol, in which it is easily soluble; it crystallises in white, lustrous needles, and melts at 152—154°. The *oxime* crystallises from alcohol in slender, white needles, melts at 210° with decomposition, and is sparingly soluble in alcohol and benzene, easily so in acetone and ether. The *phenylhydrazone* crystallises in large, yellow plates, melts at 158°, and is easily soluble in all the usual solvents.

Dibromodipiperonylacryl ketone, $(CH_2O_2{:}C_6H_2Br\cdot CH{:}CH)_2CO$, is sparingly soluble or insoluble in most solvents, crystallises from acetic acid in slender, lemon-yellow needles, and dissolves in concentrated sulphuric acid forming an intense blue solution. Both ketones are sensitive to light.

Bromopiperonyllactyl methyl ketone,

$$CH_2O_2{:}C_6H_2Br{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$$

is obtained as an intermediate product in the above condensation when bromopiperonal is dissolved in a large quantity of acetone. It is a yellowish-white, crystalline compound, melts at 110°, is insoluble in cold water, sparingly soluble in hot water, easily so in alcohol, ether, and benzene, and is converted into bromopiperonylacryl methyl ketone (m. p. 152°) when boiled with acetic acid. E. C. R.

Isomeric Paranitrobenzaldoximes. By H. GOLDSCHMIDT and C. KJELLIN (*Ber.*, **24**, 2547—2556).—α-Paranitrobenzaldoxime was prepared according to the method described by Gabriel and Herzberg (Abstr., 1883, 1104), and exhibited all the properties formerly assigned to it.

Carbanilido-α-paranitrobenzaldoxime, $NHPh{\cdot}COO{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, is obtained by warming equivalent quantities of the oxime and phenyl cyanate dissolved in benzene on the water-bath, and evaporating the solution in a vacuum. It crystallises from alcohol in yellowish-white scales, melts at 157°, and is easily soluble in hot alcohol and benzene, less so in ether, and only very sparingly in light petroleum. When warmed with soda, it is decomposed into the oxime, aniline, and carbonic acid.

α-Paranitrobenzaldoxime methyl ether, $OMe{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, is obtained by the action of methyl iodide on a mixture of equivalent quantities of the α-oxime and sodium methoxide dissolved in methyl alcohol, and is purified by distillation with steam. It crystallises in white needles, melts at 101°, and is easily soluble in cold alcohol, benzene, light petroleum, chloroform, and ether.

α-Paranitrobenzaldoxime ethyl ether is obtained in a similar way to the methyl ether; the reaction does not, however, take place so easily, and it is necessary to heat the mixture for some time on the water-bath. It crystallises in colourless, tetragonal tablets, melts at 107—108°, is easily soluble in the ordinary solvents, and is volatile with steam. When it is heated with alcohol at 200°, paranitrobenzamide, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, is formed.

β-Paranitrobenzaldoxime is obtained by passing hydrogen chloride into a dry ethereal solution of the α-oxime, and then treating with a solution of soda the hydrochloride of the β-oxime, which separates in small, white needles, and melts at 116° with decomposition. It crystallises from ethyl acetate in small, lustrous tablets, melts at 170—176°, and is sparingly soluble in cold alcohol, benzene, and chloroform, more so in hot alcohol, and dissolves in alkalis with a yellowish-red coloration.

Carbanilido-β-paranitrobenzaldoxime is obtained in lemon-yellow needles on adding phenyl cyanate to an ethereal solution of the β-oxime. It melts at 94° with evolution of gas, is easily soluble in benzene, sparingly so in cold alcohol, and is decomposed on warming with alcohol. When warmed with sodium hydroxide, it yields β-paranitrobenzaldoxime, aniline, carbonic acid, paranitrobenzonitrile, and a small quantity of diphenylcarbamide.

Methyl paranitroisobenzaldoxime, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH}<\begin{matrix}\mathrm{O}\\ | \\ \mathrm{NMe}\end{matrix}$, is obtained by the action of methyl iodide on the β-oxime and sodium methoxide dissolved in methyl alcohol. It crystallises from hot alcohol in lemon-yellow needles, melts at 205°, and is sparingly soluble in light petroleum, benzene, ether, and cold alcohol, fairly easily in hot alcohol. When boiled with hydrochloric acid, it yields paranitrobenzaldehyde and methylhydroxylamine, $\mathrm{NHMe{\cdot}OH}$. When heated with strong hydriodic acid at 120°, it yields methylamine. A small quantity of the isomeric ether, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OMe}$, is also formed in the above reaction, and is separated from the mother liquors by steam distillation.

Ethyl paranitroisobenzaldoxime, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH}<\begin{matrix}\mathrm{O}\\ | \\ \mathrm{NEt}\end{matrix}$, is obtained in a similar way to the methyl compound, together with a small quantity of the isomeric ether, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OEt}$. It crystallises from hot alcohol in lemon-yellow needles, melts at 119—120°, is easily soluble in hot alcohol and benzene, sparingly in ether, and almost insoluble in light petroleum. When boiled with hydrochloric acid, it yields paranitrobenzaldehyde and a compound which reduces Fehling's solution, and is probably $\mathrm{NHEt{\cdot}OH}$.

β-Paranitrobenzaldoxime methyl ether, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OMe}$, is obtained as follows:—The β-oxime is dissolved in the smallest quantity of soda, and silver nitrate added to the solution. The silver salt thus obtained is collected, suspended in ether, and methyl iodide added. The mixture is shaken from time to time and, after some hours, is filtered; the ethereal filtrate is washed with dilute soda, the ether distilled, and the residue crystallised from petroleum. It crystallises in spear-like needles, melts at 67—68°, and is easily soluble in the ordinary solvents.

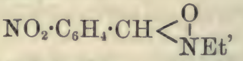
β-Paranitrobenzaldoxime ethyl ether, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OEt}$, is obtained in a similar way to the methyl compound; it crystallises from petroleum in colourless needles, melts at 70—71°, and is easily soluble in the ordinary organic solvents. When heated with alcohol at 190—200°, a product melting at 145° is obtained; on further heating, paranitrobenzamide is obtained.

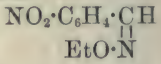
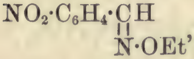
The last two β-compounds are easily converted into α-compounds by dissolving them in carbon bisulphide containing a little iodine, and heating the mixture on a water-bath.

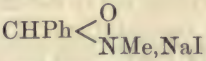
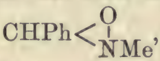
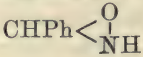
A determination of the molecular weights of the above compounds gave results agreeing with the formula $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{\cdot}NOR}$, both for the α- and β-compounds.

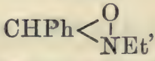
E. C. R.

Additive Compounds of Alkylisoaldoximes. By H. GOLDSCHMIDT and C. KJELLIN (*Ber.*, **24**, 2808—2817).—The *compound* $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH}<\begin{matrix}\mathrm{O}\\ | \\ \mathrm{NMe,NaI}\end{matrix}$ separates when a methyl alcoholic solution of metanitroisobenzaldoxime is mixed with sodium ethoxide and methyl iodide in molecular proportion, and the mixture concentrated, whilst methylmetanitroisobenzaldoxime, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OMe}$, melting at 72° (compare Abstr., 1890, 1262) remains in the mother liquor; the additive compound is likewise obtained when the above mixture is allowed to remain for a time, filtered from sodium iodide, evaporated to dryness, and the methylmetanitroisobenzaldoxime (m. p. 72°) extracted with ether from the residue; also when its components are heated together in a sealed tube at 100°. It forms large, yellow plates, melts at 180—185°, and is readily soluble in alcohol, but when dissolved in hot water, it is decomposed into methylmetanitroisobenzaldoxime (m. p. 117°; *loc. cit.*); benzene and ether also decompose it. It is unaltered when heated in a current of dry air at 160°, whilst at 190° methylamine passes over.

Ethylmetanitroisobenzaldoxime,  $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH}<\begin{matrix}\mathrm{O}\\|\\\mathrm{NEt}\end{matrix}$, is obtained from metanitroisobenzaldoxime, ethyl iodide, and sodium ethoxide; it crystallises from boiling water in yellowish needles, melts at 97°, and is only slightly soluble in cold water, sparingly in ether and light petroleum, readily in alcohol and hot benzene; the formation of a compound with sodium iodide was not observed here.

The two stereoisomeric *ethylmetanitrobenzaldoximes*,  $\begin{matrix}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH}\\\|\\\mathrm{EtO{\cdot}N}\end{matrix}$ and  $\begin{matrix}\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH}\\\|\\\mathrm{N{\cdot}OEt}\end{matrix}$, were also prepared; they are both oils.

The *compound*  $\mathrm{CHPh}<\begin{matrix}\mathrm{O}\\|\\\mathrm{NMe,NaI}\end{matrix}$ is produced from isobenzaldoxime, sodium ethoxide, and methyl iodide in methyl alcoholic solution; also by evaporating mixed aqueous solutions of methylisobenzaldoxime and sodium iodide in molecular proportion; it melts at 69—72°, dissolves readily in water and alcohol, is slowly decomposed by benzene and ether, and gives a brown precipitate which readily undergoes decomposition when treated with a concentrated aqueous solution of copper acetate. When an aqueous solution, to which common salt has been added, is extracted with ether, methylisobenzaldoxime,  $\mathrm{CHPh}<\begin{matrix}\mathrm{O}\\|\\\mathrm{NMe}\end{matrix}$, is obtained from the ethereal solution; on adding light petroleum to its solution in a little benzene, it separates in colourless plates; it melts at 82°, and is readily soluble in water, alcohol, and benzene, somewhat less so in ether; it decomposes when heated with dilute hydrochloric acid, and in addition to the above described sodium iodide compound, it appears to form a similar derivative with calcium chloride. Unlike isobenzaldoxime, it is not volatile, and as methyl derivatives are invariably more readily volatile than their parent substances, it would seem that isobenzaldoxime has not the constitution  $\mathrm{CHPh}<\begin{matrix}\mathrm{O}\\|\\\mathrm{NH}\end{matrix}$ previously ascribed to it.

Ethylisobenzaldoxime,  $\mathrm{CHPh}<\begin{matrix}\mathrm{O}\\|\\\mathrm{NEt}\end{matrix}$, likewise yields a compound with sodium iodide; this melts at 67—70°.

When methylisobenzaldoxime (m. p. 82°) and phenyl cyanate are dissolved in benzene in molecular proportion, and the solution, after remaining for 24 hours, evaporated, the additive compound, $C_{15}H_{14}N_2O_2$, which crystallises from alcohol in white needles and melts at 119°, is obtained; when heated with concentrated hydrochloric acid in a sealed tube at 100°, carbonic anhydride, aniline, ammonia, and benzaldehyde are formed. The *compound* $C_{16}H_{16}N_2O_2$, melting at 116—117°, is prepared from ethylisobenzaldoxime and phenyl cyanate; when heated with concentrated hydrochloric acid at 100°, it yields the same decomposition products as the methyl derivative. In like manner the compound $C_{16}H_{15}N_3O_4$, melting at 148°, is formed from ethylmetanitroisobenzaldoxime (m. p. 67°) and phenyl cyanate: whilst the compound $C_{21}H_{17}N_3O_4$, melting at 158—159°, is produced from benzylmetanitrobenzaldoxime and phenyl cyanate.

A. R. L.

Homologues of Benzhydrylamine. By H. GOLDSCHMIDT and H. STÖCKER (*Ber.*, **24**, 2797—2808).—*Paratolhydrylamine*,

$$NH_2{\cdot}CH(C_6H_4Me)_2,$$

is prepared from paraditolylketoxime (Goldschmidt, Abstr., 1890, 1412) as follows:—The ketoxime (5 grams) is treated in alcoholic solution with 2·5 per cent. sodium amalgam (105 grams) and acetic acid at 60° (compare Abstr., 1887, 249). The product is poured into water, sodium hydroxide added, and the mixture extracted with ether; on distilling the ethereal solution, a white, crystalline mass is left, from which paratolhydrylamine is extracted by boiling with light petroleum, whilst paratoluic paratoluide (Goldschmidt, *loc. cit.*) remains undissolved. It separates from light petroleum in transparent tablets, melts at 93°, and is readily soluble in ether and alcohol. The *hydrochloride*, formed by passing hydrogen chloride into a solution of the base in light petroleum, separates from water in white needles, and melts at 235°; whilst the *acetyl derivative*, $C_{15}H_{15}{\cdot}NHAc$, obtained by boiling the base with acetic anhydride, crystallises from alcohol in delicate, white needles, and melts at 159°. When a solution of potassium cyanate is added to a hot aqueous solution of the hydrochloride, *paratolhydrylcarbamide*, $CH(C_6H_4Me)_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, is produced; it separates from dilute alcohol in small, white needles, and melts at 152°.

Parahomobenzhydrylamine, $C_6H_4Me{\cdot}CHPh{\cdot}NH_2$, is obtained, together with paratoluic anilide, by reducing crude paratolylphenylketoxime (Hantzsch, Abstr., 1890, 1273) as above, employing sodium amalgam (110 grams) and the ketoxime (5 grams). The product is thrown into water, acidified with hydrochloric acid, and extracted with ether to remove the anilide; it is then rendered alkaline and again extracted with ether; on distilling the second ethereal solution, parahomobenzhydrylamine is obtained as an oil having a faint basic odour and boiling at 296° (723 mm.); it is sparingly soluble in water, cannot be solidified, and absorbs carbonic anhydride from the air. The *hydrochloride* crystallises from boiling water in quadratic prisms, and melts at 252°; the *platinochloride*, $(C_{14}H_{15}N)_2,H_2PtCl_6 + 2H_2O$, is a bright yellow, crystalline precipitate which dissolves sparingly in water, but more readily in alcohol, and melts at 119°; whilst the *acetyl derivative*, $C_{14}H_{13}{\cdot}NHAc$, crystallises from alcohol in white needles, and melts at 131°. When a solution of potassium cyanate is added to a hot aqueous solution of the hydrochloride, *parahomobenzhydrylcarbamide*, $C_6H_4Me\cdot CHPh\cdot NH\cdot CO\cdot NH_2$, separates; it crystallises from dilute alcohol in white needles, and melts at 158°. *Parahomobenzhydrylaminethiocarbamide*, $C_6H_4Me\cdot CHPh\cdot NH\cdot CS\cdot NH_2$, is obtained by treating an aqueous solution of the hydrochloride with the theoretical quantity of potassium thiocyanate, evaporating to dryness, extracting with absolute alcohol, and again evaporating; the oil thus obtained soon solidifies to reddish needles, which are rendered colourless by washing with ether; it melts at 100—101°. *Parahomobenzhydrylphenylcarbamide*, $C_6H_4Me\cdot CHPh\cdot NH\cdot CO\cdot NHPh$, is formed when phenyl cyanate is added to an ethereal solution of the base; it separates from boiling alcohol in small, white needles, and melts at 206°. Parahomobenzhydrylamine contains an asymmetric carbon atom, but, as might be anticipated, since it is a synthetical product, is optically inactive. The authors were not, however, successful in resolving it into two optically active isomerides by crystallisation of either the monodextrotartrate or of the normal salt; they also find that the same base is formed by reducing pure α-paratolylphenylketoxime (Hantzsch, *loc. cit.*) instead of the crude ketoxime, together also with paratoluic anilide. The *monodextrotartrate*, $C_{14}H_{15}N,C_4H_6O_6$, forms small, white needles, and melts at 157°; whilst the normal *dextrotartrate*, $(C_{14}H_{15}N)_2,C_4H_6O_6$, which is only produced when concentrated solutions of the acid and base are mixed in the requisite proportion, separates in white, microscopic needles, and melts at 72—73°.

Orthotolyl phenyl ketone, $C_6H_4Me\cdot COPh$, prepared from orthotoluic chloride by the method described by Elbs (Abstr., 1886, 461), for the preparation of aromatic ketones, boils at 295° (722 mm.); compare Ador and Rilliet (*Ber.*, **12**, 2301). The *oxime* forms white needles, and melts at 95—98°; it is probably a mixture of two stereochemical isomerides.

Orthohomobenzhydrylamine, $C_6H_4Me\cdot CHPh\cdot NH_2$, is formed, together with orthotoluic anilide, by reducing orthotolylphenylketoxime with sodium amalgam; the two products are isolated in the same manner as those of the para-series (see above). The new base is a colourless oil which boils at 299° (721 mm.), absorbs carbonic anhydride from the air, and is somewhat soluble in water. The *hydrochloride* begins to darken at 220°, melts at 249°, and is readily soluble in water; whilst the *acetyl* derivative crystallises from alcohol in small, white prisms, and melts at 124°.

Metatolyl phenyl ketone, prepared from metatoluic chloride, boils at 311—313° (723 mm.); compare Ador and Rilliet (*loc. cit.*); the *oxime* melts at 100—101°, and is perhaps a mixture of two stereochemical isomerides.

Metahomobenzhydrylamine, $C_6H_4Me\cdot CHPh\cdot NH_2$, is a colourless oil closely resembling its isomerides; it boils at 299° (724 mm.); the *hydrochloride* forms delicate, white needles, commences to darken at 220°, melts completely at 243°, and is fairly soluble in water; whilst the *acetyl derivative* crystallises from alcohol in colourless needles, and melts at 97°.

A. R. L.

Conversion of Gallic Acid and Tannin into Benzoic Acid. By C. E. Guignet (*Compt. rend.*, **113**, 200—201).—When a warm solution of gallic acid is added to a warm mixture of zinc powder and ammonia solution, the gallic acid is completely converted into benzoic acid after heating for some hours at 60°. A similar result is obtained by heating gallic acid with zinc and dilute sulphuric acid, except that in this case the benzoic acid remains undissolved.

Under similar conditions, tannin is first converted into gallic acid, and finally into benzoic acid. C. H. B.

Hydrogenation of Benzoic Acid. By O. Aschan (*Ber.*, **24**, 2617—2622; compare this vol., p. 1053).—*Hexahydrobenzoic acid* is obtained, together with benzoic acid, when the product of the action of hydrogen bromide on tetrahydrobenzoic acid (*loc. cit.*) is reduced with sodium amalgam. In the pure and anhydrous form, it melts at 28°, and boils at 224° under 725 mm. pressure. The *amide*, $C_6H_{11}\cdot CONH_2$, crystallises from water in large, flat prisms melting at 184°, and the *methyl* salt boils at 175—176° under 719 mm. pressure, and has a density of 1·014 at 0°/0°, and 0·9927 at 20°/20°. The acid is not affected by heating with concentrated hydrochloric acid at 170—250°, and does not seem to be identical with the author's hexanaphthenecarboxylic acid (Abstr., 1890, 737).

α-Bromhexahydrobenzoic acid, $C_6H_{10}Br\cdot COOH$, is prepared by heating the mixture of phosphorus oxychloride and the acid chloride, produced by the action of phosphorus pentachloride on hexahydrobenzoic acid, with the calculated quantity of bromine at 100—120°, and extracting the product with formic acid (sp. gr. = 1·2). It crystallises from formic acid in large, silvery scales or flat prisms, melts at 63°, has an odour of iodoform, and is unstable in the presence of boiling water and alkalis.

Δ^1-*Tetrahydrobenzoic acid* is obtained when α-bromhexahydrobenzoic acid is treated with alcoholic potash at the ordinary temperature and the product is distilled with steam. It is a colourless oil which boils at 235—236° under 718 mm. pressure, and, when cooled below 0°, solidifies to a crystalline mass melting at about 8°. Bromination takes place only slowly and incompletely when the acid is treated with bromine, and leads to the production of the two stereometric dibromides, which could not be satisfactorily separated, although they differ in solubility and crystalline form, the less soluble substance crystallising in prisms, and the more soluble in lamelliform rhombohedra. If, however, the mixture of acid chloride and phosphorus oxychloride formed by the action of phosphorus pentachloride on the acid is treated with the calculated quantity of bromine, and the brominated acid chloride converted into the acid by prolonged boiling with excess of formic acid (sp. gr. = 1·2), the less soluble dibromide of Δ^1-tetrahydrobenzoic acid is the sole product. This crystallises from concentrated formic acid, dilute acetic acid, or a mixture of benzene and light petroleum in small, prismatic forms, melts at 142°, and regenerates the tetrahydro-acid when boiled with alkalis or alkaline carbonates, or if treated in the cold with alcoholic potash.

Δ^1-*Tetrahydrobenzamide* crystallises from ether in octahedra, and melts at 127—128°.

The tetrahydrobenzoic acid obtained by the reduction of benzoic acid with sodium amalgam (*loc. cit.*), is most probably the Δ^2-acid, since, on the one hand, it yields the Δ^1-acid by boiling with strong, aqueous potash, and, on the other, its methyl salt is converted into methyl benzoate by atmospheric oxygen, reactions which, according to v. Baeyer's experience, are characteristic of hydrophthalic acids containing a "double bond" in the Δ^2-position. The action of bromine on this acid leads to the formation of only one dibromide, further examination having shown that the supposed isomeride is nothing but benzoic acid, which is almost always present in small quantity in the crude tetrahydro-acid. The pure dibromide crystallises from dilute acetic acid in lustrous, colourless scales, and melts at 166°, not at 163°. Δ^2-*Tetrahydrobenzamide* forms white, nacreous scales or prisms, melts at 144°, and is more soluble in water and ether than the amide of the Δ^1-acid.

A *dihydrobenzoic acid*, possibly the $\Delta^{1,3}$-acid, is formed by the action of concentrated alcoholic potash on the dibromide of the Δ^2-tetrahydro-acid at the ordinary temperature. It crystallises from its concentrated aqueous solution, by slow evaporation in the cold, in large, hard prisms which melt at 73°. W. P. W.

β-Dichlorhydrin Metahydroxybenzoate. By C. Göttig (*Ber.*, **24**, 2741—2743; compare this vol., p. 707).—Metahydroxybenzoic acid is dissolved in 10 parts of glycerol, the solution heated at 85°, and treated with hydrogen chloride for five hours; two compounds are formed, and may be separated by solution in hot water. The one is amorphous, and has not been further investigated; the second consists of *β-dichlorhydrin metahydroxybenzoate*, $OH\cdot C_6H_4\cdot CO\cdot OC_3H_5Cl_2$, and crystallises in long, slender needles which melt at about 90°. The constitution of the compound is proved by the fact that on hydrolysis with soda or potash, metahydroxybenzoic acid and epichlorhydrin are formed as the sole products. If the etherification of the metahydroxybenzoic acid is conducted at temperatures above 85°, the yield of the amorphous compound is proportionately increased.

J. B. T.

Optically Active Phenylbromolactic Acids and Phenoxyacrylic Acids. By E. Erlenmeyer, Jun. (*Ber.*, **24**, 2830—2831).—Optically inactive phenylbromolactic acid can be easily separated into its optically active constituents by conversion into the cinchonine salt and crystallisation from alcohol. The salt of the dextrorotatory acid crystallises almost completely from the solution when a certain concentration is reached, and the remainder can be separated by the addition of ether. The salt of the levorotatory acid is left as a viscid mass after evaporation of the alcoholic mother liquor, and can be obtained in the solid form by repeated treatment with pure ether. The optically active acids, obtained from the salts by treatment with dilute hydrochloric acid and extraction with ether, closely resemble the optically inactive acid in properties; the melting points, however, are not identical.

The sodium salts of the optically active phenoxyacrylic acids are formed when the optically active phenylbromolactic acids are treated with aqueous caustic soda. The aqueous solutions of these salts exhibit a greater rotatory power than the solutions of the phenylbromolactic acids, and, moreover, the salt derived from dextrorotatory phenylbromolactic acid rotates to the left, whilst that from the levorotatory acid rotates to the right. On treatment with sulphuric acid, both salts are converted into phenylethylaldehyde. A detailed account of the physical properties of these optically active isomerides is reserved for a later communication. W. P. W.

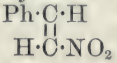
Diiodocinnamic Acid. By C. Liebermann and H. Sachse (*Ber.*, **24**, 2588—2589).—*Diiodocinnamic acid*, $CPhI{:}CI\cdot COOH$, is obtained by allowing a solution of molecular proportions of phenylpropiolic acid and iodine in carbon bisulphide to remain exposed to sunlight in a stoppered bottle. The iodine is very slowly absorbed, and is still visible after a month. The mixture deposits beautiful leaflets having a silvery lustre. It is purified by dissolving in alcohol and precipitating with water, and melts at 171°. The *sodium* salt is obtained in beautiful needles by dissolving the acid in dilute sodium carbonate, and then adding excess of the reagent. The *barium* salt is soluble; the *lead* salt forms a white precipitate. With sodium amalgam, it yields hydrocinnamic acid.

Methyl diiodocinnamate is obtained from methyl phenylpropiolate in a similar way. It is easily soluble in alcohol, and is precipitated, on the addition of water, in scales of silvery lustre, and melts at 77°.

E. C. R.

Nitration of Cinnamic Acid and Phenylmethacrylic Acid in the Side Chain. By H. Erdmann (*Ber.*, **24**, 2771—2775).—The author has previously obtained phenylnitroethylene in small quantity by the action of red fuming nitric acid on phenylisocrotonic acid (Abstr., 1884, 906). Phenylnitroethylene is also formed in very small quantity when cinnamic acid is stirred into warm, red fuming nitric acid; in larger quantity when an ethereal solution of the acid, cooled in a bath of ice and salt, is saturated with nitrous gas obtained by the action of arsenious anhydride on nitric acid, and to the extent of 15 per cent. of the theoretical, when a mixture of the acid (20 grams) with 10 per cent. aqueous sodium nitrite (100 c.c.) is distilled with steam.

Phenylnitropropylene is obtained when a cold, ethereal solution of phenylmethacrylic acid is treated with nitrous gas, and a volatile product of aromatic odour is formed in very small quantity from phenylangelic acid under like conditions.

Two stereometric forms of phenylnitroethylene are conceivable, and the author is of opinion that the formula  $\begin{array}{c} Ph\cdot C\cdot H \\ \| \\ H\cdot C\cdot NO_2 \end{array}$ is the more probable for the compound produced in the above reactions. This view seems to derive some confirmation from the fact that all attempts to reduce orthonitrophenylnitroethylene to cinnoline have been fruitless.

W. P. W.

Condensation of Allocinnamic Acid with Phenols. By C. Liebermann and A. Hartmann (*Ber.* **24**, 2582—2587).—The following method of condensation is employed:—Finely powdered allocinnamic acid (10 grams) is dissolved in phenol (10 grams) and acetic acid (5 c.c.); the mixture cooled and mixed with strong sulphuric acid (10 c.c.) diluted with acetic acid (5 c.c.). After remaining four days, the viscid mass is poured into water, and extracted with ether. The ethereal solution is shaken with water to get rid of acetic acid, and then extracted with soda, and finally the ether is distilled off. An oil is thus obtained which has a phenolic odour, and gradually solidifies; it is then spread on porous plates to remove adhering oil. If a crystal of the substance thus obtained be added to the oil from later experiments, it at once solidifies. The substance is phenylhydrocoumarin. The soda solution contains hydroxydiphenylpropionic acid.

Hydroxydiphenylpropionic acid, $C_{15}H_{14}O_3$, is obtained from the above soda solution by acidifying and extracting with ether. It is very soluble in alcohol, crystallises from benzene in plates, and melts at 151°. The *ammonium* salt loses ammonia on evaporation of its solution. Lead acetate and silver nitrate cause white precipitates when added to solutions of the ammonium salt. The *calcium* and *barium* salts are very soluble. The author puts forward two formulæ for the compound,

$$OH\cdot C_6H_4\cdot CHPh\cdot CH_2\cdot COOH \text{ and } OH\cdot C_6H_4\cdot CH(CH_2Ph)\cdot COOH,$$

of which he considers the former to be the more probable. The acid is not converted into phenylhydrocoumarin when heated at 160°.

Phenylhydrocoumarin, $C_{15}H_{12}O_2$, an indifferent compound, is insoluble in soda, dissolves easily in alcohol, and on the addition of water is obtained in beautiful, colourless needles; it crystallises from light petroleum in rosettes of needles, melts at 82°, and distils at 237° under a pressure of 30 mm., for the most part without decomposition. When boiled with alkali, it dissolves, and on adding an acid to the solution a white compound is precipitated, which is only partly soluble in soda, as it rapidly changes into phenylhydrocoumarin.

Phenylhydroxyhydrocoumarin, $C_{15}H_{12}O_3$, is obtained by condensation of allocinnamic acid with resorcinol by the method described above. It is easily soluble in most solvents, almost insoluble in light petroleum, and quite so in water, gives a yellow solution with soda or ammonia, and a yellow lead salt on the addition of lead acetate to the ammoniacal solution.

The condensation of cinnamic acid with phenol does not give good results under the above conditions. The condensation was effected by heating cinnamic acid (5 grams), phenol (5 grams), sulphuric acid (7 grams), and acetic acid (7 grams) on the water-bath for an hour. From the product, phenylhydrocoumarin was obtained, identical with that obtained from allocinnamic acid. The condensation takes place very slowly in the cold.

E. C. R.

Amidobenzoic Derivatives of Ethyl Acetoacetate. By G. Pellizzari (*Gazzetta*, **21**, 340—345).—It has been shown by Knorr (Abstr., 1887, 159) and Conrad and Limpach (Abstr., 1887, 679;

Ber., **22**, 78) that aromatic amines generally react in two ways with ethyl acetoacetate according to the conditions of the experiment. The author investigates these reactions in the case of amidobenzoic acid.

Ethyl hydrogen ac-metacrotonamidobenzoate, $C_{13}H_{15}NO_4$, is obtained by boiling a solution of metamidobenzoic acid (10 grams) and ethyl acetoacetate (10 grams) in 96 per cent. alcohol (20 grams) for one hour; on cooling, the whole solidifies to a crystalline mass, which, after recrystallisation from alcohol, is obtained in beautiful, colourless prisms melting at 137°. It is very soluble in alcohol and ether, and on prolonged heating in aqueous solution breaks up into its constituents, the yield of amidobenzoic acid being quantitative. It has probably the constitution $COOEt{\cdot}CH{:}CMe{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$. Attempts to eliminate alcohol and obtain a quinoline derivative, as may be done in analogous cases, did not succeed.

ac-Acetylacetometamidobenzoic acid, $COMe{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}COOH$, is obtained by directly heating a mixture of equivalent proportions of metamidobenzoic acid and ethyl acetoacetate; the semi-fluid mass is extracted with ether to remove the unaltered constituents, and recrystallised from alcohol; it is then obtained in colourless crystals very soluble in hot alcohol and acetic acid, moderately so in water, and melting with decomposition at 172—173°. The *silver salt* is a white powder. On endeavouring to prepare a quinoline derivative by heating the acid with concentrated sulphuric acid, nothing but amidobenzoic acid sulphate was obtained. *Acetylacetorthamidobenzoic acid* is obtained in a manner quite analogous to the meta-acid as white needles melting with decomposition at 160°. It is moderately soluble in hot alcohol and water, less so in benzene, and only sparingly in ether. W. J. P.

Action of Phthalic Chloride on Phenols. By R. MEYER (*Ber.*, **24**, 2600; see also this vol., p. 1029).—Ethereal salts of phthalic acid are usually formed by the action of phthalic chloride on phenols, and not phthaleïns or their anhydrides; for instance, phenyl phthalate has been prepared by this method. Paracresol and pseudocumenol also yield the corresponding ethereal salts, which are very well crystallised compounds. β-Naphthol and phthalic chloride yield, as the chief product, naphthyl phthalate, together with a compound which melts above 200°, dissolves in sulphuric acid with an intense reddish-yellow fluorescence, and is evidently the anhydride of β-naphtholphthaleïn. The author reserves a full description of the compounds for a future communication. E. C. R.

Relationship between Ethyl Succinosuccinate and Phloroglucinol. By A. v. BAEYER (*Ber.*, **24**, 2687—2690).—The author and Kochendörfer have previously shown that phloroglucinol combines with 2 mols. of phenylhydrazine yielding a dihydrazine derivative (Abstr., 1889, 1162); the formation of this compound may be explained by assuming that the triketohexamethylenedihydrazone first produced undergoes intramolecular change.

Ethyl succinosuccinate shows a behaviour similar to that exhibited by phloroglucinol, and with phenylhydrazine gives a hydrazine derivative of dihydroterephthalic acid (compare following abstracts). Now, since diketohexamethylene, the parent substance of succinosuccinic acid, behaves like a true diketone (compare Baeyer and Noyes, Abstr., 1889, 1147), its conversion into a phenol, analogous to phloroglucinol, in the reaction just referred to, must be due to the presence of the carboxyethyl groups. The fact that a hydroxy-derivative of dihydrobenzene, which shows all the properties of a phenol, can be obtained by simple substitution in the nucleus is of fundamental importance with regard to the benzene theory; for, if in dihydrobenzene the double binding which, on the introduction of a hydroxyl-group, is converted into a single binding with formation of a ketone (in accordance with Erlenmeyer's rule), attains the character of the double binding in phloroglucinol simply owing to the presence of a carboxyethyl group, there is no reason to deny the probability of other substitutions or other changes in the molecule giving a stability to the double binding similar to that observed in the case of benzene derivatives. The objection might be raised that the stability of the double binding in ethyl succinosuccinate is due to the fact that the substituting groups are in the para-position to one another; such a view is negatived by the observation of Baeyer and Tutein (Abstr., 1889, 1180) that hydroxytetrahydroterephthalic acid behaves just like succinosuccinic acid. F. S. K.

Phenylhydrazine Derivatives of Ethyl Succinosuccinate. By A. v. Baeyer, R. Jay, and L. Jackson (*Ber.*, **24**, 2690—2691).—*Ethyl parabenzenedihydrazo-*$\Delta^{2:5}$*-dihydroterephthalate*, $C_{24}H_{28}N_4O_4$, is formed, together with the isomeric $\Delta^{1:4}$-compound, when finely divided ethyl succinosuccinate (5 grams) is warmed with phenylhydrazine (4·2 grams) and alcohol (15 grams) until solution is complete; after keeping the mixture for 3 to 4 days, the crystals are separated by filtration, and extracted with boiling alcohol, from which, on cooling, the $\Delta^{2:5}$-derivative is deposited in colourless needles. It turns yellow at 135—140°, sinters together at 145°, melts at 165° with decomposition, and is soluble in 15 parts of boiling alcohol; it is unstable towards acids and alkalis, and dissolves in cold, concentrated mineral acids, and in acetic acid and formic acid yielding red solutions; its solution in propionic acid has a reddish hue, but it dissolves in valeric acid yielding a colourless solution which, on heating, suddenly turns yellow, crystals of the $\Delta^{1:4}$-compound being deposited. When heated alone or in alcoholic solution, it is converted into the isomeride described below.

Ethyl parabenzenedihydrazo-$\Delta^{1:4}$-dihydroterephthalate (Knorr and Bülow's ethyl diphenylizinsuccinosuccinate), $C_{24}H_{28}N_4O_4$, prepared as described above, is very sparingly soluble in all ordinary solvents and can be easily purified by extraction with boiling alcohol; it is a yellow, microscopic, crystalline powder, melts at 208°, and behaves like the $\Delta^{2:5}$-derivative on treatment with acids and alkalis.

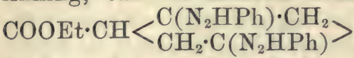
F. S. K.

Constitution of the Phenylhydrazine Derivatives of Ethyl Succinosuccinate. By A. v. Baeyer and G. v. Brüning (*Ber.*, **24**, 2692—2699).—*Ethyl benzenebiazo-$\Delta^{2:5}$-dihydroterephthalate*, $C_{24}H_{24}N_4O_4$, can be obtained in yellow needles by gradually adding a hot, saturated alcoholic solution of normal copper acetate (7 grams), acidified with a little acetic acid, to a boiling alcoholic solution of the $\Delta^{2:5}$-hydrazo-compound described in the preceding abstract, and then dropping the filtered solution on to ice; it melts at 155°, is readily soluble in alcohol and other ordinary solvents, and dissolves in concentrated hydrochloric acid and concentrated sulphuric acid, yielding red solutions. It is much more stable than the $\Delta^{2:5}$-hydrazo-compound; on reduction, it is converted into the $\Delta^{1:4}$-hydrazo-derivative, intramolecular change taking place.

Ethyl benzenebiazoterephthalate, $C_{24}H_{22}N_4O_4$, is formed, with liberation of hydrogen bromide, when bromine is added to an alcoholic solution of the preceding compound; it crystallises from alcohol in long, lustrous, orange-red needles and melts at 126°. It resembles the dihydrazo-derivative in appearance, but is more readily soluble in alcohol and much more stable. The corresponding *acid*, $C_{20}H_{14}N_4O_4$, prepared by hydrolysing the ethyl salt with boiling concentrated potash, crystallises from a mixture of glacial acetic acid, water, and alcohol in orange-red needles, melts above 250°, and is readily soluble in alcohol and other organic solvents, but insoluble in water. The *silver* salt, $C_{20}H_{12}N_4O_4Ag_2$, is a dark-red, crystalline powder.

Ethyl benzenebiazo-$\Delta^{1:4}$-dihydroterephthalate, $C_{24}H_{24}N_4O_4$, is formed when the corresponding dihydrazo-compound (compare preceding abstract) is oxidised with copper acetate as described above, but the solution must be boiled for a much longer time, owing to the insolubility of the hydrazo-compound; the $\Delta^{1:4}$-biazo-derivative is also formed, together with varying quantities of the corresponding $\Delta^{2:5}$-compound, from which it is produced by intramolecular change, when the $\Delta^{2:5}$-dihydrazo-derivative is oxidised with copper acetate in presence of water. It crystallises from alcohol in light-yellow needles, melts at 180°, and is more sparingly soluble than its isomeride; it dissolves in hydrochloric acid with a red coloration, and, on reduction, it is converted into the $\Delta^{1:4}$-dihydrazo-compound. When treated with bromine in chloroform solution, the colour of the mixture changes from brown to red and crystals of a bromo-derivative, melting at 253—254°, are deposited; if, however, a solution of the azo-compound in concentrated sulphuric acid is treated with bromine, ethyl benzenebiazoterephthalate, identical with the compound described above, is obtained.

The isomerism of the two compounds obtained by the action of phenylhydrazine on ethyl succinosuccinate is caused by a difference in the constitution of the dihydroterephthalic acids of which they are derivatives. It has been previously shown that, on careful reduction, terephthalic acid is first converted into the readily soluble $\Delta^{2:5}$-dihydro-acid, which, when boiled with soda, is transformed into the sparingly soluble, stable $\Delta^{1:4}$-dihydro-derivative; in an exactly analogous manner, ethyl succinosuccinate gives, in the first place, the colourless, unstable hydrazo-derivative, which is readily converted into the yellow, stable, insoluble isomeride.

Now, in accordance with theory, three isomeric benzenebihydrazodihydroterephthalic acids, namely the $\Delta^{2:5}$-, $\Delta^{1:5}$-, and $\Delta^{1:4}$-compounds, differing from one another only as regards the position of the double linking, can be derived from a hydrazone of the constitution  $COOEt\cdot CH<{C(N_2HPh)\cdot CH_2 \atop CH_2\cdot C(N_2HPh)}>CH\cdot COOEt$, the hypothetical primary product of the action of phenylhydrazine on ethyl succinosuccinate; since the $\Delta^{2:5}$-compound may, theoretically, exist in two forms, the maleïnoïd and the fumaroïd, a fourth isomeride is also capable of existence. The only two isomerides which have yet been obtained show the same relation to one another as that existing between the fumaroïd $\Delta^{2:5}$- and the $\Delta^{1:4}$-dihydroterephthalic acids; it may be assumed, therefore, at any rate provisionally, that they have the constitutions assigned to them above.

This investigation affords an interesting contribution to the question of the relation between colour and constitution; the above facts show that, by a slight change in the position of the double linking, a yellow compound may become colourless, and *vice versâ.*

F. S. K.

Sulphonation of Parachloronitrobenzene and Parachloraniline. By A. Claus and C. Mann (*Annalen*, **265**, 87—95).—*Chloronitrobenzenesulphonic acid* [Cl : SO_3H : NO_2 = 1 : 2 : 4] is best prepared by adding parachloronitrobenzene to 10—12 per cent. anhydrosulphuric acid (6 parts) and then heating the mixture at 120—130° until it is completely soluble in dilute alkali; no other sulphonic acid is formed even when the conditions of the experiment are altered. It separates from water in well-defined, almost colourless, asymmetric crystals, $a : b : c = 0.8584 : 1 : 0.8520$, containing 2 mols. H_2O, both of which are expelled at 110°; it is readily soluble in water, but only very sparingly in alcohol. The *ammonium* salt, with $1H_2O$, *sodium* salt, with $1H_2O$, and the *potassium* salt (anhydrous) are crystalline compounds, readily soluble in water, but only sparingly in alcohol. The *barium* salt (anhydrous), *calcium* salt, with $8H_2O$, *copper* salt, with $5H_2O$, and *lead* salt, with $7H_2O$, are readily soluble in hot water and crystallise well. The *chloride*, $NO_2\cdot C_6H_3Cl\cdot SO_2Cl$, crystallises from ether in yellowish prisms melting at 89—90° (uncorr.). The *amide*, $NO_2\cdot C_6H_3Cl\cdot SO_2\cdot NH_2$, crystallises in colourless, lustrous needles and prisms, melts at 185—186° (uncorr.), and is readily soluble in ether, chloroform, alcohol, and hot water.

Chloramidobenzenesulphonic acid [Cl : SO_3H : NH_2 = 1 : 2 : 4], prepared by reducing the preceding compound with tin and boiling dilute hydrochloric acid, crystallises from hot water in colourless, prismatic needles. The *barium* salt, with $6H_2O$, is almost insoluble in alcohol, but very readily soluble in hot water, from which it separates in small needles. The *stannochloride* crystallises in large, lustrous prisms.

Two isomeric sulphonic acids are formed when parachloraniline sulphate is mixed with 15 per cent. anhydrosulphuric acid (8 parts), the mixture heated on the water-bath for 6—8 hours, and then poured into a large volume of water; the yield of the mixed products is small. On fractionally crystallising the mixture of acids from hot water, a chloramidobenzenesulphonic acid, identical with the compound just described, is first deposited, and from the mother liquors the isomeride [$Cl : SO_3H : NH_2 = 1 : 3 : 4$] is obtained in short, oblong, efflorescent prisms, containing 2 mols. H_2O. F. S. K.

Sulphonation of Metachloronitrobenzene and Metachloraniline. By A. CLAUS and H. BOPP (*Annalen*, **265**, 95—107).—The authors can confirm the statement of Post and Meyer (*Ber.*, **14**, 1605), that two isomeric sulphonic acids are obtained on heating metachloronitrobenzene with anhydrosulphuric acid at 125° for several hours. Post and Meyer's α-acid, isolated in the manner described by them, has the constitution [$SO_3H : NO_2 : Cl = 1 : 3 : 5$], and is formed in larger quantities the more concentrated the anhydro-acid employed. The corresponding *chloride*, $NO_2{\cdot}C_6H_3Cl{\cdot}SO_2Cl$, is an oil; the *amide*, $NO_2{\cdot}C_6H_3Cl{\cdot}SO_2{\cdot}NH_2$, crystallises from alcohol and water in small, colourless plates melting at 164—165° (uncorr). The constitution of this acid was proved to be that given above by first reducing it to the corresponding chloramidosulphonic acid described by Post and Meyer (*loc. cit.*); this compound was then converted into metachlorobenzenesulphamide by first eliminating the amido-group and then treating the product with phosphorus pentachloride and anhydrous ammonia consecutively. Another portion of the chloramidosulphonic acid was treated with sodium amalgam to eliminate the chlorine, and the resulting amidosulphonic acid transformed into the corresponding chlorosulphonic acid by means of the diazo-compound; this substance was finally converted into the sulphamide, which was found to be identical with the metachlorobenzenesulphamide obtained in the first case.

The second acid, obtained by sulphonating metanitrochlorobenzene as described above, has the constitution [$SO_3H : NO_2 : Cl = 1 : 2 : 6$]; its *chloride*, $NO_2{\cdot}C_6H_3Cl{\cdot}SO_2Cl$, crystallises from ether in yellow prisms, melts at 180°, and is sparingly soluble in chloroform; the corresponding *amide*, $NO_2{\cdot}C_6H_3Cl{\cdot}SO_2{\cdot}NH_2$, crystallises from water in long, colourless needles, and decomposes at a high temperature, but without melting. The constitution of this sulphonic acid was determined by the same methods as those employed in the case of the isomeride.

At least two, possibly four, isomeric sulphonic acids are formed when metachloraniline sulphate is heated for 10—12 hours on the water-bath with anhydrosulphuric acid (3—4 parts); on treating the product with water, and precipitating the sulphuric acid with barium hydroxide, there remains in solution a mixture of barium salts which cannot be easily resolved into its constituents, but from which, by fractionally crystallising the free acids from water, pure metachloranilinesulphonic acid [$SO_3H : NH_2 : Cl = 1 : 2 : 4$] and an impure isomeride can be obtained. The former has been previously described by Post and Meyer; its constitution was determined by the authors by the same methods as those used in the case of the nitrochlorobenzenesulphonic acids. The impure isomeride has, most probably, the constitution [$SO_3H : Cl : NH_2 = 1 : 2 : 4$]. F. S. K.

Sulphonation of Orthotoluidine. By A. Claus and F. Immel (*Annalen*, **265**, 67—87).—Orthotoluidinemetasulphonic acid

$$[NH_2 : Me : SO_3H = 1 : 2 : 5]$$

is formed in considerable quantity, together with the isomeride $[NH_2 : Me : SO_3H = 1 : 2 : 4]$, when ortholuidine sulphate (1 part) is mixed with 50 per cent. anhydrosulphuric acid (2 parts) cooled below 0°, and the mixture kept at this temperature with frequent shaking until it has become a thick, brown mass; the product is then treated with ice-cold water, the cold solution neutralised with barium carbonate, and the barium salts in the filtered solution separated by fractional crystallisation from water. With regard to the 1 : 2 : 4-acid, it may be remarked that the statements of Gerver on this subject are incorrect, but those of Neville and Winther (*Ber.*, **13**, 1941) correct; when treated with bromine (1 mol.) in glacial acetic acid solution, it is converted into a crystalline bromo-derivative

$$[NH_2 : Me : SO_3H : Br = 1 : 2 : 4 : 6],$$

the barium salt of which crystallises with 3 mols. H_2O; when this bromo-acid is treated with bromine (1 mol.) in aqueous solution, it yields dibromotoluidine (m. p. 50°), the platinochloride of which crystallises with $1\frac{1}{2}$ mols. H_2O. Orthotoluidinemetasulphonic acid, prepared from the barium salt, is very readily soluble in water, from which it crystallises in colourless, transparent needles, containing 1 mol. H_2O; it is doubtless identical with the acid obtained by the reduction of nitrotoluenesulphonic acid (compare Hayduck, *Annalen*, **172**, 204). The *sodium* salt, with $3H_2O$, crystallises in needles, and is very readily soluble in water and alcohol. The *barium* salt, with $2\frac{1}{2}H_2O$, crystallises in rhombic plates, and is more readily soluble in water than the corresponding salt of the isomeric acid referred to above. The *calcium* salt, with $6H_2O$, the *cobalt* salt, and the *nickel* salt are crystalline and readily soluble in water. When the acid is treated with bromine in aqueous solution, it is converted into a dibromo-derivative $[NH_2 : Me : Br_2 : SO_3H = 1 : 2 : 4 : 6 : 5]$, which crystallises from boiling water in long, colourless needles, containing 1 mol. H_2O (compare Hayduck, *loc. cit.*); the barium salt of this bromo-acid crystallises from hot water with $8\frac{1}{2}$ mols. H_2O.

Tribromotoluenesulphonic acid $[Br_3 : Me : SO_3H = 1 : 4 : 6 : 2 : 5]$ can be obtained by decomposing the diazo-derivative of the dibromo-acid just described with cuprous bromide (compare Hayduck, *Annalen*, **174**, 354); it crystallises from hot water in small, colourless prisms, and, when treated with highly superheated steam in concentrated sulphuric acid solution, it is readily decomposed into tribromotoluene (m. p. 53°).

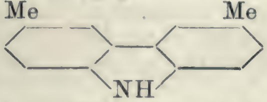
Paratoluidinemetasulphonic acid $[NH_2 : SO_3H : Me = 1 : 3 : 4]$ is formed in large quantities when paratoluidine is sulphonated under the conditions described in the case of the corresponding ortho-compound; the product is washed with cold water to free it from small quantities of the orthosulphonic acid, and then crystallised from hot water, from which it separates in well-defined rhombohedra containing 1 mol. H_2O. It is insoluble in alcohol, reduces ammoniacal silver nitrate solution, and gives a red coloration on warming with ferric chloride; when boiled with excess of bromine in aqueous solution, it yields a *tribromoparatoluidine*, [$NH_2 : Br_3 : Me = 1 : 2 : 3 : 6 : 4$], which crystallises in colourless needles melting at 83° (uncorr.).

When aniline sulphate is sulphonated in the cold in the manner described above, the parasulphonic acid alone is obtained; orthobromaniline also gives but one sulphonic acid, which is identical with the compound [$NH_2 : Br : SO_3H = 1 : 2 : 5$] described by Andrews (*Ber.*, **13**, 2126). F. S. K.

Bromisatin-blue. Compounds of Mono- and Di-bromisatin with Piperidine. By C. SCHOTTEN (*Ber.*, **24**, 2604—2607).—*Dipiperidylbromisatin*, $C_{18}H_{24}BrN_3O$, is obtained by warming an alcoholic solution of bromisatin with twice the molecular proportion of piperidine. It crystallises in colourless needles, is very sparingly soluble in alcohol, and closely resembles dipiperidylisatin in its behaviour with acids, alkalis, and on warming (compare this vol., p. 928).

Bromisatin-blue is formed when dipiperidylbromisatin is warmed with several times its weight of acetic anhydride, and, on the addition of water to the blue solution is precipitated as a microcrystalline powder. It resembles isatin-blue (*loc. cit.*) in its behaviour with solvents, acids, and alkalis.

Piperidinedibromisatin, $C_{13}H_{14}Br_2N_2O_2$, is obtained by adding piperidine to dibromisatin suspended in warm, absolute alcohol. It crystallises in short, pale-yellow prisms, melts at 152°, dissolves sparingly in alcohol, but more easily in ether, and is insoluble in water. It is not affected by boiling with dilute mineral acids or alkalis, or with acetic acid or acetic anhydride, but decomposes with the regeneration of dibromisatin when heated with a mixture of hydrochloric and acetic acids. W. P. W.

Dimethylcarbazole. By E. TÄUBER and R. LOEWENHERZ (*Ber.*, **24**, 2597—2599).—The paper contains a further account of the dimethylcarbazole 

formerly described by the authors (this vol., p. 834). Dimethylcarbazole can be prepared in two ways, from diamidodimethylcarbazole, and by heating orthodiamidoditolyl with a mineral acid above 200°. The first method gives very bad results; the second method is also disadvantageous owing to the difficulty of preparing large quantities of orthodinitroditolyl.

Orthodinitroditolyl is best obtained as follows:—Well dried metadinitrotolidine is made into a paste with a little absolute alcohol and the calculated quantity of 100 per cent. sulphuric acid (for 2 mols.), poured into 15 times as much absolute alcohol, and amyl nitrite (2 mols.) added to the mixture at 10°. The mixture is then heated for some hours to boiling, diluted with water, and the orthodinitroditolyl extracted with high boiling petroleum. The nitro-product is reduced with tin and hydrochloric acid, and the diamido-hydrochloride (m. p. 83°) thus obtained is converted into dimethylcarbazole by heating it with six times the quantity of hydrochloric acid (18 per cent.) in a sealed tube at 230° for 20 hours.

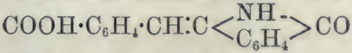
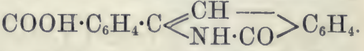
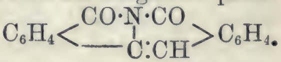
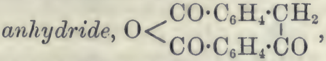
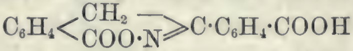
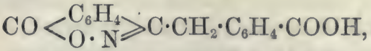
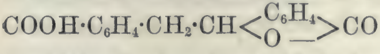
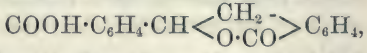
Dimethylcarbazole crystallises from benzene in colourless needles, melts at 219°, is easily soluble in hot benzene, toluene, and alcohol, somewhat easily in ether and carbon bisulphide, and sparingly so in light petroleum, and is very like ordinary carbazole. The *picric acid compound* crystallises in reddish-brown needles, and melts at 192°. The *nitroso*-compound crystallises from alcohol in pure, yellow needles, and melts at 106°. The *acetyl* compound crystallises from alcohol in needles, and melts at 129°. A wood splinter soaked in an alcoholic solution of dimethylcarbazole is coloured red by hydrochloric acid; with isatin, its solution in sulphuric acid gives an indigo-blue. It is distinguished from carbazole by not giving a blue dye on fusion with oxalic acid. When shaken with quinone in acetic acid solution containing a few drops of concentrated sulphuric acid, it gives a deep, indigo-blue solution, and this, on the addition of water, deposits greyish-blue flocks, which dissolve in ether with a bluish-violet colour. Carbazole, under the same treatment, gives a magenta solution, which, on the addition of water, yields reddish-brown flocks, soluble in ether to a red liquid. A table is given of the properties of carbazole and dimethylcarbazole. E. C. R.

Preparation of Hydrobenzoïn and of Deoxybenzoïn. By P. JUILLARD and G. TISSOT (*Chem. Centr.*, 1891, ii, 166; from *Arch. sci. phys. nat. Genève*).—The authors recommend the following method for the preparation of hydrobenzoïn; the product is very pure, but the amount is small: 100 grams of benzaldehyde is reduced with 100 grams of zinc-dust in 500 grams of glacial acetic acid and 10 grams of anhydrous acetic acid. After the zinc-dust has been gradually added, the mixture is heated at 100° for 1½ hours. The resulting liquid is diluted with 4—5 volumes of water and the hydrobenzoïn precipitated with sodium carbonate. It crystallises in beautiful plates, and melts at 134°. The yield is 5—10 per cent. From the oily residue, a few white crystals separated at the end of a few days; the remainder was principally benzyl alcohol and deoxybenzoïn. If dilute acetic acid be employed for the reduction, the product consists chiefly of benzyl alcohol.

Deoxybenzoïn is prepared by the reduction of benzoïn or acetylbenzoïn as follows:—40 grams of benzoïn and 40 grams of zinc are treated with 200 grams of glacial acetic acid, and the reduction is almost perfect. Neither hydrobenzoïn nor acetylhydrobenzoïn is found among the products. Acetylbenzoïn was prepared by heating 2 grams of benzoïn with 10 grams of anhydrous acetic acid for four hours in a tube at 150°, whereby the theoretical quantity was obtained. It crystallises in white needles, and melts at 83°. J. W. L.

Derivatives of Deoxybenzoïn. By J. EPHRAIM (*Ber.*, **24**, 2820—2827).—*Deoxybenzoïnorthodicarboxylic acid*,

$$COOH\cdot C_6H_4\cdot CO\cdot CH_2\cdot C_6H_4\cdot COOH,$$

is obtained by heating 1 : 2-carboxyphenylacetic acid (10 parts) with an equal weight of phthalic anhydride, and sodium acetate (1 part) in an oil-bath at 180—190°, the reagents being anhydrous, treating the dark-coloured melt with hot water, dissolving in cold sodium hydroxide solution, precipitating the filtrate with hydrochloric acid, treating the precipitate with cold alcohol, and crystallising from glacial acetic acid; it forms white needles and melts at 238—239°; the *silver* salt separates in white, feathery needles on adding silver nitrate to a solution of the ammonium salt. When the acid (2 grams) is heated with fuming hydriodic acid (5 c.c.) and amorphous phosphorus (1 gram) in a sealed tube at 160° for 2—3 hours, and the melt extracted with sodium carbonate solution, dibenzylorthodicarboxylic acid, $C_2H_4(C_6H_4\cdot COOH)_2$, melting at 225°, separates on the addition of hydrochloric acid. The *acid*, $C_{16}H_{11}O_3N$, is formed when deoxybenzoïnorthodicarboxylic acid (1 gram) is heated with concentrated alcoholic ammonia in a sealed tube for 12 hours; it crystallises from alcohol in white rhombohedra, and its constitution is represented either by  $COOH\cdot C_6H_4\cdot CH{:}C\genfrac{<}{>}{0pt}{}{NH-}{C_6H_4}CO$ or by  $COOH\cdot C_6H_4\cdot C\genfrac{<}{>}{0pt}{}{CH—}{NH\cdot CO}C_6H_4$. This, when heated on the water-bath with twice its weight of phosphorus oxychloride, yields the *compound*,  $C_6H_4\genfrac{<}{>}{0pt}{}{CO\cdot N\cdot CO}{—C{:}CH}C_6H_4$. When deoxybenzoïnorthodicarboxylic acid is dissolved in absolute alcohol, the cooled solution saturated with hydrogen chloride, and water added, the *anhydride*,  $O<\begin{matrix}CO\cdot C_6H_4\cdot CH_2\\ CO\cdot C_6H_4\cdot CO\end{matrix}$, is precipitated; it crystallises from alcohol in white needles, melts at 260°, and is insoluble in cold alkalis. The *oximidolactone*,  $C_6H_4\genfrac{<}{>}{0pt}{}{CH_2—}{COO\cdot N}C\cdot C_6H_4\cdot COOH$ or  $CO\genfrac{<}{>}{0pt}{}{C_6H_4}{O\cdot N}C\cdot CH_2\cdot C_6H_4\cdot COOH$, is produced when the acid is dissolved in alkali and treated with hydroxylamine; it crystallises from alcohol in delicate, rose-coloured needles, and melts at 229—230°; the *lactone*,  $COOH\cdot C_6H_4\cdot CH_2\cdot CH\genfrac{<}{>}{0pt}{}{C_6H_4}{O—}CO$ or  $COOH\cdot C_6H_4\cdot CH\genfrac{<}{>}{0pt}{}{CH_2-}{O\cdot CO}C_6H_4$, is obtained when the acid is treated with five times the calculated quantity of sodium amalgam in alkaline solution; it separates from alcohol in monosymmetric crystals, $a : b : c = 0{\cdot}8962 : 1 : 0{\cdot}7478$; $\beta = 61° 43'$, and melts at 201°. The *barium salt* of the bibasic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot C_6H_4\cdot COOH$, is formed when the lactone is boiled with barium hydroxide, and, on adding the silver nitrate to the resulting solution, the *silver salt* is precipitated.

The author has separated a small quantity of a bye-product, $C_{16}H_{10}O_4$, in the preparation of deoxybenzoïnorthodicarboxylic acid by the above-described method; it crystallises from glacial acetic acid in white needles, melts at 250°, and is not identical with deoxybenzoïnorthodicarboxylic anhydride. It yields an acid, $C_{16}H_{12}O_5$, melting at 196°, which thus appears to be isomeric with deoxybenzoïnorthodicarboxylic acid. A. R. L.

Synthesis of Hydroxyxanthones. By B. NESSLER (*Chem. Centr.*, 1891, ii, 61; from *Schweiz. Wochenschr. Pharm.*, **29**, 186).—Similarly to the formation of xanthone from orthohydroxybenzoic acid, hydroxyxanthones may be prepared from dihydroxy-acids. From dihydroxybenzoic acid, dihydroxyxanthone is formed; from a mixture of salicylic and dihydroxybenzoic acids, a monohydroxyxanthone is obtained; and the phenols, resorcinol, orcinol, quinol, and phoroglucinol unite with hydroxy-acids with formation of corresponding hydroxyxanthones.

J. W. L.

Derivatives of Lapachic Acid. By E. PATERNÒ and L. CABERTI (*Gazzetta*, **21**, 374—381).—Monobromolapachic acid may be reduced by suspending it in very dilute caustic potash and treating with zinc dust; after half an hour, the solution is filtered, saturated with carbonic anhydride, and, as soon as the resin is deposited, the liquid is filtered and acidified with hydrochloric acid, when a flocculent precipitate of lapachic acid falls. This shows Hooker and Green's opinion, that monobromolapachic acid is a derivative of lapachone (Abstr., 1889, 999), is incorrect.

Paternò and Minunni (Abstr., 1890, 1310) showed that lapachic acid, when treated with thiophen and sulphuric acid, yields a condensation product; the authors find that the reaction occurs between the thiophen and lapachone formed by the action of sulphuric acid on the lapachic acid. Lapachone (1 part) and thiophen (1 part) are dissolved in glacial acetic acid (1 vol.) and concentrated sulphuric acid (1 vol.) added; after five hours, the emerald-green solution is poured into much water, the bulky, blue precipitate collected and washed, first with water, then with a mixture (equal parts) of alcohol and water, and finally dried. The substance is now of an intense, sky-blue colour, and is soluble in strong alcohol, ether, chloroform, and light petroleum, yielding a blue solution; it dissolves in acetic acid and in sulphuric acid, from which it is precipitated by water, a part being resinified. In solution this substance seems to be unaltered by hydrochloric acid or sodium amalgam, but is slowly oxidised by nitric acid and at once decolorised by chlorine-water. It contains sulphur, but could not be obtained sufficiently pure for quantitative analysis.

On passing dry hydrogen chloride through a solution of lapachic acid in glacial acetic acid, the solution becomes brownish-red, and, on pouring it into water, yields lapachone and a trace of another substance, probably the compound obtained when lapachic acid is treated with nitric acid. If a solution of lapachone and thiophen in glacial acetic acid is saturated with dry hydrogen chloride and allowed to remain for some days, the blue compound described above is obtained. A solution of lapachic acid (1 part) in glacial acetic acid, on treatment with fused zinc chloride (10 parts), yields nothing but pure lapachone after remaining for 18 hours. Zinc chloride also effects the condensation of lapachone with thiophen, but much resinous matter is produced at the same time. Lapachic acid is partially converted into lapachone by calcium chloride, but is seemingly unaltered by stannous chloride in alcoholic solution.

An improved process for the preparation of lapachic acid is the following:—The crude product (100 grams), obtained by boiling the shavings or sawdust of lapacho wood with sodium carbonate, and decomposing the solution with hydrochloric acid, is boiled with baryta-water (30—35 grams barium hydrate in 15 litres of water). On filtration and precipitation with hydrochloric acid, the lapachic acid is generally pure enough to be at once recrystallised from alcohol.

W. J. P.

Melting Points of Binary Systems of Hydrocarbons. By L. VIGNON (*Compt. rend.*, **113**, 133—136).—The hydrocarbons employed were naphthalene, diphenyl, phenanthrene, triphenylmethane, and anthracene, which were mixed in pairs in various proportions.

The mixtures may be divided into two groups, namely, (*a*) those that contain anthracene and have a melting point which rises as the proportion of anthracene increases, but is always higher than the mean calculated melting point; and (*b*) those that contain no anthracene. In the latter group, the melting point is always lower than the mean calculated melting point, and the curves have a characteristic form, showing a point of reversal which corresponds in the various cases to the following mixtures: naphthalene, 2 mols., and diphenyl, 1 mol.; naphthalene, 2 mols., and phenanthrene, 1 mol.; naphthalene, 1 mol., and triphenylmethane, 1 mol.; diphenyl, 2 mols., and phenanthrene, 1 mol.; diphenyl, 2 mols., and triphenylmethane, 1 mol.

C. H. B.

Truxillic Acids. By J. HOMANS, R. STELTZNER, and A. SUKOW (*Ber.*, **24**, 2589—2592).—When α-truxillic acid is treated with a small quantity of fuming nitric acid (1·52), it dissolves, and two isomeric mononitro-acids are formed. The one acid (*b*) crystallises from the solution on cooling, the other (*a*) is obtained by diluting with water and is purified by crystallisation from alcohol.

a-Nitro-α-truxillic acid, $[C_9H_7(NO_2)O_2]_2$, forms small prisms, melts at 228—229°, and is easily soluble in alcohol, ether, and acetic acid, sparingly in benzene. It is not attacked by potassium permanganate in alkaline solution, and is thus distinguished from nitrocinnamic acid. The salts do not crystallise. *Ethyl a-nitro-α-truxillate* crystallises from alcohol in yellow needles and melts at 138°.

b-Nitro-α-truxillic acid is insoluble, or only sparingly soluble, in all solvents, melts at 290° with decomposition, and does not reduce permanganate. The *silver* salt forms a white, granular precipitate. The *barium* salt is easily soluble in water and crystallises in bright-yellow needles.

β- and γ-truxillic acids each yield only one mononitro-acid.

Nitro-β-truxillic acid is, when first obtained, an oil which is purified with difficulty by recrystallisation from alcohol. It melts at 216°, is easily soluble in ether, acetic acid, and chloroform, sparingly in benzene, and does not reduce potassium permanganate.

Nitro-γ-truxillic acid forms small prisms, melts at 293°, is easily soluble in alcohol and acetic acid, insoluble in benzene, and slowly reduces potassium permanganate.

The amido-derivatives of α-truxillic acid are obtained by reducing the nitro-derivatives with tin and hydrochloric acid, precipitating the tin with sulphuretted hydrogen, and concentrating the filtrate in a vacuum on the water-bath.

a-Amido-α-truxillic acid is obtained, in scales of silvery lustre, by precipitating a solution of the hydrochloride with sodium acetate, and is purified by precipitation from acetone by petroleum. The *hydrochloride* forms very soluble needles.

b-Amido-α-truxillic acid crystallises from water in needles. The *hydrochloride* forms needles, and is less soluble than the *a*-amido-acid. The *sulphate* is obtained in beautiful, sparingly soluble needles on adding the theoretical quantity of sulphuric acid to a solution of the hydrochloride.

b-Diazo-α-truxillic acid nitrate, $[C_9H_7(N_2NO_3)O_2]_2$, is obtained in pale-yellow needles by adding sodium nitrite (1·84 grams) to an ice-cold solution of the hydrochloride of the amido-acid (5 grams) in a small quantity of water and nitric acid (5 c.c.). It is easily soluble in water, and yields a ponceau-red dye with sodium β-naphtholdisulphonate, which does not, however, dye cotton directly.

b-Hydroxy-α-truxillic acid is obtained by adding the calculated quantity of sodium nitrite to a solution of the amido-hydrochloride in concentrated sulphuric acid. The mixture is diluted with water and heated to boiling, when the hydroxy-acid is obtained as a yellow precipitate. It crystallises from alcohol in colourless flocks, is sparingly soluble in most solvents, does not melt at 360°, dissolves in cold soda, and is precipitated by acids. The *calcium* salt is obtained by boiling the acid with calcium carbonate, is easily soluble in water, and is precipitated on the addition of alcohol.

b-Acetylhydroxy-α-truxillic acid is obtained by the action of acetic anhydride and sodium acetate on the hydroxy-acid; it crystallises from acetic acid in tufts of needles, and melts at 244°. E. C. R.

Essence of Lemons. By V. OLIVERI (*Gazzetta*, **21**, 318—330).—Recently prepared essence of lemons is a canary-yellow, oily liquid, of a pungent acrid taste. Its sp. gr. is 0·860 at 16°, and its specific rotatory power $[\alpha]_D$ at 16° varies from $+69·75°$ to $+75·10°$.

On distilling essence of lemons which has been steam-distilled and dried over fused potassium carbonate, three principal fractions are obtained. The first portion, boiling at 170—170·5°, constitutes about one-fifteenth part of the whole, and has a sp. gr. of 0·8867 at 0° and a specific rotatory power $[\alpha]_D = +64·82°$ at 16°. It is a colourless, mobile liquid, having the characteristic odour of the essence, and has the composition of a terpene, $C_{10}H_{16}$.

Limonene Tetrabromide, $C_{10}H_{16}Br_4$.—This is obtained when the limonene (1 vol.) is dissolved in a mixture of alcohol (4 vols.) and ether (4 vols.), and bromine (0·7 vol.) dropped into the solution cooled to 0°. The product, after washing with cold alcohol and dissolving in boiling ethyl acetate, is obtained as an oil which, after a time, solidifies to a crystalline mass melting at 31°. The *dihydrochloride*, $C_{10}H_{18}Cl_2$, is prepared by passing excess of hydrogen chloride through a mixture of equal weights of ether and the limonene; the ether is evaporated, and the product dried on a porous plate and recrystallised from alcohol. It forms small, colourless, six-sided tables melting at

50°; it agrees in properties with the dihydrochloride prepared by Wallach.

The second fraction from lemon oil boils between 176° and 178° and includes about nine-tenths of the whole; it is a mobile, colourless liquid having a sp. gr. of 0·8990 at 0° and a specific rotatory power $[\alpha]_D = +76·75°$. Vapour density determinations and analyses show it to have the composition $C_{10}H_{16}$. The *tetrabromide*, $C_{10}H_{16}Br_4$, prepared as above, melts at 102—103°; the *dihydrochloride*, $C_{10}H_{18}Cl_2$, crystallises in scales soluble in alcohol, and melts at 50°.

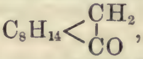
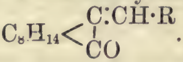
The third fraction boils at 240—242°; in fresh lemon oil, the proportion is very small, but much larger quantities are obtained from old oil, along with polyterpenes boiling at 250—340°. The portion boiling at 240—242° consists of a sesquiterpene, $C_{15}H_{24}$; it is a viscous, yellowish liquid, of sp. gr. = 0·9847 at 0°, very slowly volatile with steam, and optically inactive. It is soluble in ether, and sparingly soluble in alcohol. The *tetrabromide*, $C_{15}H_{24}Br_4$, is a heavy, colourless oil, which does not solidify at −20°. The *dihydrochloride*, $C_{15}H_{26}Cl_2$, separates from its cooled alcoholic solution as an oil.

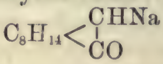
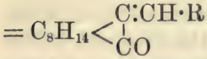
Detection of Oil of Turpentine as an Adulterant in Essence of Lemons.—The sophistication of essence of lemons by turpentine oil is difficult to detect, owing to the percentage composition of the two oils being identical and their boiling points and densities being almost the same.

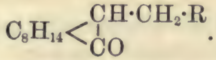
The author finds that the readiest method of detecting the fraud is to observe the specific rotatory power. As the adulterant most frequently employed is French turpentine oil, having a specific rotatory power of $[\alpha]_D = -27·0°$ about, its presence in lemon oil, having a specific rotation $[\alpha]_D = +60·0°$, is at once betrayed; the amount of the adulterant may be easily calculated, as the rotatory power of the mixture is the algebraic sum of the rotatory powers of its constituents taken in the proportions in which they are present. Even when the adulterant is a dextrorotatory oil, such as Russian or English turpentine, the change in the rotatory power is so great as to at once betray its presence.

The author gives tables for calculating the percentage of the adulterant present from its rotatory power. W. J. P.

Hygroscopic Behaviour of Camphor and Thymol. By G. Clautriau (*Ber.*, **24**, 2612—2614).—In the course of the physiological investigation of the irritability of a fungus, Errara arrived at the conclusion that camphor has a considerable hygroscopic capacity which is not shared by thymol. This view is confirmed by the author's experiments. A small, tared vessel containing camphor was supported in the middle of a glass receiver of 3 litres capacity, which was closed by a cover smeared with camphorated lard. To avoid loss of camphor by evaporation, the walls of the receiver were completely covered with a layer of camphor, and the water employed to keep the air moist was also saturated with camphor. Similar precautions were adopted in the case of thymol. After deducting the weight of water found to condense on the tared vessel in a blank experiment, numbers were obtained indicating that 10 grams of camphor absorbed 0·022 and 0·032 gram of water in two experiments, whilst thymol showed no appreciable increase in weight. Dry camphor, although it attracts a comparatively small amount of water, does so with such energy that its weight increases even in air containing but little moisture. On the other hand, the condensed water is readily removed, even under the influence of less moist camphor. W. P. W.

Compounds of Camphors with Aldehydes. By A. HALLER (*Compt. rend.*, **113**, 22—26).—If the constitution of camphor is correctly represented by the formula  $C_8H_{14}<\begin{matrix}CH_2\\ |\\ CO\end{matrix}$, it may be expected to form, with aldehydes, condensation products having the general formula  $C_8H_{14}<\begin{matrix}C{:}CH{\cdot}R\\ |\\ CO\end{matrix}$.

After various unsuccessful or only partially successful attempts to verify this idea, it was found that many aldehydes react with sodium-camphor according to the general equation  $C_8H_{14}<\begin{matrix}CHNa\\ |\\ CO\end{matrix}$ + R·CHO  $= C_8H_{14}<\begin{matrix}C{:}CH{\cdot}R\\ |\\ CO\end{matrix}$ + NaOH, and that the substances thus obtained furnish reduction products having the general formula



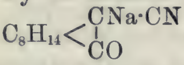
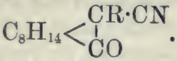
$$C_8H_{14}<\begin{matrix}CH{\cdot}CH_2{\cdot}R\\ |\\ CO\end{matrix}.$$

Benzalcamphor, $C_{10}H_{14}O{:}CHPh$, is obtained by treating sodium-camphor with benzaldehyde. Camphor (150 grams) dissolved in toluene (400 grams) is heated with sodium (15 grams) in a reflux apparatus until the metal is dissolved, and the benzaldehyde (105 grams) is added to the cooled and washed product. The resulting liquid is washed with water and dried, the toluene is distilled off, and the residue is heated as long as camphor volatilises. The benzalcamphor separates from the alcoholic extract in brilliant prisms. It melts at 95—96°, and is soluble also in ether, benzene, and toluene. It exists in three physically isomeric modifications, dextrorotatory and lævorotatory, prepared respectively from dextrorotatory and lævorotatory camphor, and racemic, prepared by mixing equal proportions of the active varieties. The racemic modification melts at 78°. Benzalcamphor, when reduced with sodium amalgam, yields *benzylcamphor*, $C_{10}H_{15}O{\cdot}CH_2Ph$, which resembles, optically, the modification from which it is prepared.

Cuminalcamphor, $C_{10}H_{14}O{:}CH{\cdot}C_6H_4Pr$, prepared in a similar way from cumaldehyde, forms long, brittle prisms, soluble in the same menstrua as benzalcamphor. It melts at 62°, and is dextrorotatory. On reduction, it yields *cuminylcamphor*, $C_{10}H_{15}O{\cdot}CH_2{\cdot}C_6H_4Pr$, a yellow, oily liquid which boils between 280° and 290° under a pressure of 50 mm.

Cinnamalcamphor, $C_{10}H_{14}O{:}CH{\cdot}CH{:}CHPh$, was obtained as a yellowish, viscous, uncrystallisable liquid, boiling at 280° under a pressure of 50 mm.

Methylsalicylalcamphor, $C_{10}H_{14}O{:}CH{\cdot}C_6H_4{\cdot}OMe$, separates from alcohol in beautiful crystals melting at 92—94°. On reduction, it yields *methylsaligenylcamphor*, $C_{10}H_{15}O\cdot CH_2\cdot C_6H_4\cdot OMe$, which crystallises from alcohol in white, rhomboïdal plates, and melts at 49°. The corresponding ethyl compounds were also prepared. Jn. W.

Derivatives of Cyanocamphor. By A. Haller (*Compt. rend.*, **113**, 55—59).—Sodiumcyanocamphor,  $C_8H_{14}<\begin{matrix}CNa\cdot CN\\ |\\ CO\end{matrix}$ (*Compt. rend.*, **112**, 1477), reacts with alkyl iodides and acid chlorides to form derivatives having the general formula  $C_8H_{14}<\begin{matrix}CR\cdot CN\\ |\\ CO\end{matrix}$.

To prepare the alkyl derivatives, cyanocamphor (1 mol.) is mixed in a reflux apparatus with the alkyl iodide (rather more than 1 mol.); potash (1 mol.), dissolved in its own weight of water, is then gradually added from a tap funnel, and the whole is heated for an hour. The excess of the iodide having been distilled off, the upper oily layer of the residual liquid is treated with aqueous potash to dissolve any undecomposed cyanocamphor, and is then extracted with ether. The dry ethereal solution is evaporated, and the residual, oily product is rectified in a vacuum.

To prepare the acid derivatives, an alcoholic solution of sodium cyanocamphor is treated in the cold with the theoretical amount of an ethereal solution of the acid chloride, and the reaction is completed with the aid of heat. The product is then taken up with water and extracted with ether, and the ethereal solution is washed with aqueous potash, dried, and allowed to evaporate. The residue consists of a solution of the acid derivative in the ethyl salt of the acid, from which crystals of the former separate after a time.

The alkyl and acid derivatives of cyanocamphor thus obtained are colourless, oily liquids, or crystalline solids, soluble in alcohol, ether, and hydrocarbons, but insoluble in water and alkalis.

Methylcyanocamphor is a liquid, which smells of grass, and boils at 170—180° under a pressure of 36 mm. Its molecular rotatory power is $[\alpha]_D = +107\cdot69°$. (The determinations of the rotatory power of the various derivatives were made on toluene solutions containing $\frac{1}{2}$ gram-mol. per litre.)

Ethylcyanocamphor is a liquid, which smells of grass and hydrocyanic acid, and boils at 163—165° under a pressure of 21 mm. Its molecular rotatory power is $[\alpha]_D = +120\cdot71°$.

Normal propylcyanocamphor crystallises in needles and has an aromatic smell and fresh taste. It melts at 46°, and boils at 150° under a pressure of 20 mm. Its molecular rotatory power is $[\alpha]_D = +126\cdot16°$.

Benzylcyanocamphor melts at 58—59°. Its molecular rotatory power is $[\alpha]_D = +93\cdot62°$.

Orthonitrobenzylcyanocamphor melts at 104—105°. Its molecular rotatory power is $[\alpha]_D = +68\cdot37°$.

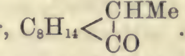
Benzoylcyanocamphor crystallises in thin, rectangular plates, and melts at 105°. It is decomposed by strong aqueous potash into potassium-cyanocamphor and potassium benzoate.

Orthotoluylcyanocamphor forms hard crystals, which are larger than those of its homologue. Jn. W.

Methyl and Ethyl Methylcamphocarboxylates. Preparation of Methylcamphor. By J. MINGUIN (*Compt. rend.*, **112**, 1369—1372).—The methyl camphocarboxylate used was a colourless oil boiling at 155—160° under a presssure of 15 mm. Its rotatory power in alcohol $[\alpha]_D = +61\cdot90°$.

Methyl Methylcamphocarboxylate.—Methyl camphocarboxylate (30 grams) and methyl iodide (25 grams) are boiled together for about two hours in a reflux apparatus with the addition of five or six portions of 20—30 c.c. of methyl alcohol in which 3·2 grams of sodium has been dissolved. Water is added and the precipitate taken up with ether. The ethereal solution, on evaporation, yields colourless crystals, soluble in alcohol, but more so in ether. The yield is about 15 grams of the pure product. There remains an oily liquid distilling at the same temperature as the camphocarboxylate and still containing, after distillation, a certain quantity of this solid. Methyl methylcamphocarboxylate melts at 85°; its rotatory power in alcohol ($\frac{1}{2}$ mol. per litre) is $[\alpha]_D = +17\cdot25°$.

Ethyl methylcamphocarboxylate is similarly prepared. It is a crystalline substance melting at 60—61°, soluble in alcohol and ether, and has a rotatory power $[\alpha]_D = +13\cdot8°$.

Methylcamphor,  $C_8H_{14}<\begin{matrix}CHMe\\ |\\ CO\end{matrix}$.—The methylcamphocarboxylates described above are not hydrolysed by treatment during four days with alcoholic potash in a reflux apparatus, but the change is readily brought about by heating in sealed tubes at 130—140°. Water is added to the contents of the tubes and the precipitate taken up with ether. The wash water contains potassium carbonate; the ethereal solution washed, dried, and evaporated, gives a crystalline substance having the odour of camphor and melting at 37—38°. Its rotatory power (1 mol. in 1 litre of alcohol) is $[\alpha]_D = 270\cdot65$.

The oily residue is hydrolysed in a reflux apparatus, when the camphocarboxylic ether is readily converted into camphor and a further quantity of the substituted ethers is obtained. W. T.

Reduction of Apione. By G. CIAMICIAN and P. SILBER (*Ber.*, **24**, 2608—2612).—Dibromapione (Abstr., 1888, 1100) is best prepared by rapidly adding the calculated quantity of bromine to a warm solution of apiolic acid in acetic acid, and immediately pouring the product into water. After addition of some sulphurous acid, the dibromapione is filtered, and purified by crystallisation from alcohol. The yield amounts to 20 grams from 13 grams of apiolic acid.

Apione (Abstr., 1888, 848) can be prepared with advantage by reduction of dibromapione, and as a small proportion of the phenol obtained by reducing apione is also formed in the reaction, the two reductions can be carried on in the same operation. Dibromapione is dissolved in 20 parts of alcohol and the boiling solution gradually saturated with sodium. The product is then diluted with twice its volume of water, distilled on a water-bath to remove alcohol, and the recovered apione again treated with sodium and boiling alcohol, the process being repeated several times until all is reduced. The alkaline liquors from each reaction are shaken out with ether to remove any dissolved apione, then acidified, and the reduction product extracted with ether, which is subsequently removed by distillation. The reduction product of apione, a dimethoxyhydroxybenzene, $C_6H_3(OMe)_2 \cdot OH$, is a thick oil, which slowly solidifies in a freezing mixture, melts at 24°, boils at 251—252°, and has a pronounced phenolic odour. With concentrated soda and potash solutions, it forms salts which crystallise in needles and dissolve easily in water. The *acetyl* derivative, $C_6H_3(OMe)_2 \cdot OAc$, crystallises from alcohol in large, colourless forms, and melts at 68°. When heated with hydrochloric acid at 100°, charring occurs, and methyl chloride is obtained, together with a crystalline compound which forms an acetyl derivative melting at about 166°. On methylation in the usual way, the reduction product is converted into a trimethoxybenzene, $C_6H_3(OMe)_3$, boiling for the most part at 248°; this, although it solidifies but slowly in a freezing mixture, melts at 14°, and, moreover, does not seem to yield a nitro-derivative, is regarded by the author as possibly identical with Will's 1 : 2 : 4-trimethoxybenzene (Abstr., 1888, 457). Further experiments to decide this question are promised. W. P. W.

Adonin, a Glucoside from Adonis amurensis. By Y. TAHARA (*Ber.* **24**, 2579—2582).—The author has prepared the glucoside from *Adonis amurensis* in order to compare it with adonidin, the glucoside from *Adonis vernalis*. The following method of extraction was used. The air-dried root (1·7 kilograms) was cut fine and extracted five times with 90 per cent. alcohol. On distilling off the alcohol, a brown mass was obtained which dissolved in water. The concentrated aqueous solution was made strongly alkaline and extracted with chloroform, the chloroform distilled off, and the residue dissolved in alcohol and fractionally precipitated with ether. In this way a yellowish, gummy mass was obtained which yields a white powder. The yield amounts to 1·94 per cent. on the material extracted. This glucoside the author calls adonin. On analysis, it gave numbers corresponding with the formula $C_{24}H_{40}O_9$.

Adonin is easily soluble in water, alcohol, chloroform, and acetic acid, insoluble in ether. The aqueous solution has a very bitter taste. It dissolves in concentrated nitric acid with an indigo blue colour; the same coloration is obtained on adding nitric acid to the acetic acid solution; with concentrated sulphuric acid it gives a deep red, with hydrochloric acid a rose-red. In aqueous solution, it is easily decomposed by mineral acids, and a few drops of hydrochloric acid in the cold convert it into a sugar and a resinous substance easily soluble in ether. Acetic acid and alkalis do not, however, decompose it. The aqueous solution is precipitated by gallic acid, picric acid, Meyer's reagent, gold chloride, &c. On shaking with benzoic chloride and potassium hydroxide, it gives a benzoyl derivative. Its toxic action is similar to that of adonidin, but is weaker. E. C. R.

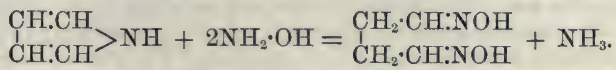
Action of Methyl Alcohol on Pyrroline. By M. DENNSTEDT (*Ber.*, **24**, 2559—2563).—The author has examined the products obtained when a mixture of methyl alcohol and pyrroline is passed over heated zinc dust. The product consists of an oil together with a small quantity of a compound which crystallises in the cooler parts of the tube, and is probably a tripyrrylmethane derivative; the latter dissolves in alcohol and acetic acid to a dark-red solution, and dyes wool and silk brown. The oil was fractionally distilled, the different fractions heated in sealed tubes with acetic anhydride and sodium acetate at 180—190°, and the products examined. The fraction boiling below 135° contained unaltered pyrroline, aldehydic and ketonic condensation products of methyl alcohol, and a very small quantity of 1-methylpyrroline. The fractions 137—140° and 142—143° gave a mixture of acetylmethylpyrrolines which distils at 230—240° and is partially solid. The solid compound which is the main product melts at 86°, and on condensation with benzaldehyde gives 2-methylpyrryl cinnamyl ketone melting at 193—194°. The oily product yields 3-methylpyrryl cinnamyl ketone melting at 148—149°. The greater part of the product is contained in the fraction boiling at 147—149°, and consists of 2-methylpyrroline, which yields the acetyl compound melting at 86°. From the last fractions, a compound was obtained which the author believes to be 2 : 3-dimethylpyrroline, together with a trimethylpyrroline.

Ethyl alcohol and pyrroline yield as chief product the ethylpyrroline boiling at 163—165°.

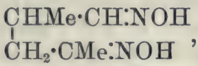
The author has also prepared the dimethylindole from the methylpyrroline boiling at 147—148°, and finds that it readily yields an acetyl compound when heated with acetic anhydride and sodium acetate at 190°. This *acetyldimethylindole* crystallises from dilute alcohol, melts at 215—217°, and is not altered by boiling with dilute alkali. The author thinks that the formation of this acetyldimethylindole is evidence that the methylpyrrol boiling at 147—148° is 3-methylpyrroline. E. C. R.

Action of Hydroxylamine on the Pyrrolines. By G. Ciamician and C. U. Zanetti (*Gazzetta*, **21**, 231—247).—*Succinazone* (*succinodiphenyldihydrazone*), $C_2H_4(CH{:}N_2HPh)_2$, prepared by treating a boiling aqueous solution of the oxime with an acetic acid solution of phenylhydrazine, crystallises from boiling alcohol in yellow scales, and melts at 124—125°.

Diphenyldipyridazine, $C_{20}H_{20}N_4$, is prepared by treating the previous compound (6 grams) in the cold with concentrated hydrochloric acid (100 c.c.) and precipitating the solution with water. It crystallises from ethyl acetate in tufts of white or yellowish needles, and melts at 184—185° with decomposition. It dissolves readily in benzene and boiling ethyl acetate, sparingly in ethyl alcohol, and is almost insoluble in light petroleum. It is a feeble base and dissolves in concentrated acids without decomposition, but is reprecipitated from its solutions by water. On treating its sulphuric acid solution with a crystal of potassium dichromate, an intense blue coloration is obtained. It probably has a constitution analogous to that of Ach's dimethyldiphenyldipyridazine (*Annalen*, **253**, 44). On treating an alcoholic solution of 1-ethylpyrroline with hydroxylamine hydrochloride and sodium carbonate, succinaldoxime and ethylamine are formed. From this, the authors conclude that the action of hydroxylamine on pyrroline may be rigorously represented by the equation



$$\left.\begin{array}{l}\mathrm{CH{:}CH}\\ |\\ \mathrm{CH{:}CH}\end{array}\right>\mathrm{NH} + 2\mathrm{NH_2{\cdot}OH} = \begin{array}{l}\mathrm{CH_2{\cdot}CH{:}NOH}\\ |\\ \mathrm{CH_2{\cdot}CH{:}NOH}\end{array} + \mathrm{NH_3}.$$

α-Methyllevulindioxime,  $\begin{array}{l}\mathrm{CHMe{\cdot}CH{:}NOH}\\ |\\ \mathrm{CH_2{\cdot}CMe{:}NOH}\end{array}$, prepared by boiling an alcoholic solution of 2 : 4′-dimethylpyrroline with hydroxylamine hydrochloride and sodium carbonate, crystallises when pure from ether in pale-yellowish needles or prisms, melts at 87—90°, dissolves in water and alcohol, and sparingly in ether, and has the general properties of an oxime. It readily reduces an alkaline copper solution and ammoniacal silver nitrate. The sodium derivative, $C_6H_{10}Na_2N_2O_2$, is a whitish powder which deliquesces in the air.

αβ′-Dimethyltetramethylenediamine,

$$\mathrm{NH_2{\cdot}CH_2{\cdot}CHMe,CH_2{\cdot}CHMe{\cdot}NH_2},$$

is obtained by reducing a solution of α-methyllevulindioxime in absolute alcohol with metallic sodium. It is a colourless, fuming liquid with a penetrating disagreeable odour, and boils at 175°. The *oxalate*, $C_4H_6Me_2(NH_2)_2,H_2C_2O_4$, crystallises in slender needles melting at 244°, with decomposition. It is hygroscopic and very soluble in water. The *platinochloride*, $(C_6H_{16}N_2),H_2PtCl_6$, forms small, orange-coloured crystals very soluble in boiling water. The *aurochloride* crystallises in tufts of yellow needles.

Acetophenoneacetonedioxime, $\mathrm{CPh(NOH){\cdot}[CH_2]_2{\cdot}CMe{:}NOH}$, prepared by the action of hydroxylamine on 2 : 5′-methylphenylpyrroline, crystallises when pure in small, white needles, melts at 108°, and dissolves in alcohol, acetic acid, and ethyl acetate, but is almost insoluble in water and light petroleum. It is readily soluble in solutions of the alkalis, but is reprecipitated by dilute acids.

S. B. A. A.

Pyridyl Ketones. By C. Engler (*Ber.*, **24**, 2525—2527).—The ketone derivatives of pyridine have been little studied hitherto, on account of the difficulty experienced in obtaining them in quantity; in view, however, of the close relations existing between these compounds and the alkaloïds, the author has subjected them to further investigation. The results obtained up to the present are given in the following abstracts.

H. G. C.

Methyl α-Pyridyl Ketone. By C. Engler and P. Rosumoff (*Ber.*, **24**, 2527—2529).—All attempts to obtain this ketone by the action of acetic chloride on pyridine in presence of aluminium chloride were without success. It was therefore prepared by distilling calcium picolinate with a slight excess of calcium acetate; a portion of the crude distillate was treated with phenylhydrazine or its sulphonic acid, the condensation product reconverted into the ketone, and the boiling point of the latter determined. The remainder of the crude product was then purified by fractional distillation.

Methyl α-pyridyl ketone, $C_5NH_4\cdot COMe$, is a colourless liquid, which boils at 192° (uncorr.), has a very characteristic odour, and becomes yellow in the air. The *hydrochloride* and *sulphate* form deliquescent masses, the *platinochloride* is a sparingly soluble crystalline powder, and the *dichromate* forms orange-yellow crystals. The *picrate* crystallises from alcohol in yellow needles melting at 131°, the *mercurochloride* melts at 150°, the *methiodide* at 161°, the *ethiodide* at 205°, and the *chloriodo-additive product* at 116°.

The *oxime*, $C_5NH_4\cdot CMe\colon NOH$, is obtained by mixing the ketone with fused hydroxylamine hydrochloride, adding aqueous soda, and gently warming. It crystallises from a mixture of ether and light petroleum in white needles, and melts at 120°. The *phenylhydrazone*, $C_5NH_4\cdot CMe\colon N_2HPh$, forms beautiful, yellow crystals, and melts at 155°; the *phenylhydrazonesulphonic acid* is obtained as a yellow precipitate by boiling the ketone with an aqueous solution of phenylhydrazinesulphonic acid, and is purified by repeated solution in ammonia and reprecipitation by acids; it does not melt at 300° and is insoluble in neutral solvents. To reconvert it into the ketone, it must be boiled with hydrochloric acid, mixed with ferric chloride to oxidise the hydrazine, and saturated with caustic soda, the solution being then extracted with ether.

On reduction with sodium amalgam, the ketone yields a solid pinacone, and a liquid pyridinalkine. The products of the action of sodium have not been isolated. H. G. C.

Ethyl α-Pyridyl Ketone and its Conversion into Pseudoconhydrine. By C. ENGLER and F. W. BAUER (*Ber.*, **24**, 2530—2536). —*Ethyl α-pyridyl ketone* is obtained in a manner similar to the methyl base by distilling a mixture of calcium picolinate and propionate, and is a characteristic smelling liquid, which boils at 205° (uncorr.) and quickly becomes brown in the air; it is soluble in alcohol, ether, and acids, but almost insoluble in water. It yields a deliquescent *hydrochloride*, a crystalline *platinochloride*, and also an *aurochloride*, a *chromate*, and a *picrate*. The *mercurochloride*, $C_8H_9NO,HgCl_2$, may be crystallised from mercuric chloride solution; the *methiodide* and *ethiodide* are obtained by heating the base with the alkyl iodide and alcohol in a sealed tube, the latter compound melting at 160°; the *chloriodo-additive product* melts at 124°. The *oxime*, $C_5NH_4\cdot CEt\colon NOH$, forms needles melting at 106°, and yields an *acetyl* and a *benzoyl* derivative melting at 46° and 69° respectively. The *phenylhydrazone*, $C_5NH_4\cdot CEt\colon N_2HPh$, crystallises in pale-yellow needles, and melts at 142°; the *phenylhydrazonesulphonic acid* forms yellow or reddish crystals, and melts at 268°.

By the action of sodium amalgam, the ketone yields a mixture of two products; one of these separates in crystalline flakes, which increase in quantity on the addition of water, and may be recrystallised from alcohol. It consists of the *pinacone of ethyl α-pyridyl ketone*, $C_2Et_2(C_5NH_4)_2(OH)_2$; this forms white needles, melts at 135—136°, and yields a *platinochloride*, $C_{16}H_{20}N_2O_2,H_2PtCl_6 + H_2O$, which readily loses its water of crystallisation. The filtrate from the pinacone, after further treatment with sodium amalgam at 30—40°, yields the second product of the reduction, which may be extracted with ether, and consists of *α-ethylpyridylalkine*, $C_5NH_4·CHEt·OH$; it is a thick, yellowish oil which boils at 213—216°, very readily undergoes oxidation in the air, and forms a *platinochloride*,

$$(C_8H_{11}NO)_2,H_2PtCl_6,$$

crystallising in yellow prisms.

Different results are obtained by reducing the ketone with sodium in amyl alcohol solution. The fractions of the crude product boiling between 190—250° all solidify more or less on cooling, and the solid compound, after freeing from adhering oil and recrystallising from light petroleum, forms white needles which melt after sublimation at 99—100°; it has the composition $C_8H_{17}NO$, and from its mode of preparation must be *α-ethylpiperylalkine*, $C_5NH_{10}·CHEt·OH$. It has in all its properties the strongest possible resemblance to the *pseudoconhydrine* obtained by Merck from *Conium maculatum*, and further examined by Ladenburg and Adam (this vol., p. 1119). There is indeed a difference of 2° in the melting point, but this may be due to the fact that the synthetical compound is an optically inactive variety. On further reduction, it is converted into coniine.

The light petroleum mother liquors from α-ethylpiperylalkine contain another crystalline substance which melts at 68—69°, and is being further examined.
H. G. C.

Propyl α-Pyridyl Ketone. By C. Engler and H. Majmon (*Ber.*, **24**, 2536—2538).—*Propyl α-pyridyl ketone*, $C_5NH_4·COPr^a$, is obtained by distilling a mixture of calcium picolinate and butyrate, and is a colourless liquid, which boils at 216—220°, does not solidify at −20°, and assumes a greenish colour on exposure to air. Its salts are mostly deliquescent; the *platinochloride* forms yellow, crystalline plates almost insoluble in water and alcohol, the *mercurochloride* melts at about 78°, the *methiodide* at 79°, and the *chloriodo-additive product* at 85°. The *oxime*, $C_5NH_4·CPr^a:NOH$, crystallises from light petroleum in long, white needles, melts at 48°, and yields a *benzoyl* derivative melting at 56—57° (uncorr.). The *phenylhydrazone* forms yellowish-white, lustrous needles, and melts at 82°, and the *phenylhydrazonesulphonic acid* beautiful, yellow needles melting at 251° (uncorr.).

Sodium amalgam readily acts on the ketone, and yields a mixture of the *pinacone*, $C_{18}H_{24}N_2O_2$, and of *α-propylpyridylalkine*,

$$C_5NH_4·CHPr^a·OH.$$

The former crystallises from alcohol in white, lustrous needles, and melts at 146° (uncorr.); the latter was only obtained in small quantity, and is an oil, the boiling point of which lies between 212° and 224°.
H. G. C.

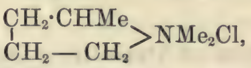
β-Ketone Derivatives of Pyridine. By C. Engler (*Ber.*, **24**, 2539—2542).—*Ethyl β-pyridyl ketone*, $C_5NH_4·COEt$, is prepared by distilling a mixture of calcium nicotinate with a slight excess of calcium propionate. It is isolated from the crude distillate by means of phenylhydrazine, the hydrazone being decomposed by boiling hydrochloric acid, the precipitated hydrochloride filtered off, and the remaining phenylhydrazine destroyed by the careful addition of potassium nitrite. The liquid is then saturated with alkali, extracted with ether, the ethereal solution evaporated, and subjected to fractional distillation. The ketone is thus obtained as a pale-yellow liquid which boils at 230—232°, and darkens on remaining in the air. The *platinochloride* forms golden-yellow crystals, and the *picrate* yellow needles; the *mercurochloride*, $C_8H_9NO,HgCl_2$, may be crystallised from a dilute mercuric chloride solution, and melts at 130°. The *oxime*, $C_5NH_4\cdot CEt\colon NOH$, crystallises in white needles, and melts at 115°; the *hydrazone*, $C_5NH_4\cdot CEt\colon N_2HPh$, in yellow needles melting at 145° (uncorr.), and the *hydrazonesulphonic acid* in pale-yellow needles melting at 235° (uncorr.).

Propyl β-pyridyl ketone, $C_5NH_4\cdot COPr^{\alpha}$, is obtained in a similar manner from calcium nicotinate and butyrate, and is an almost colourless liquid boiling at 246—252°, the odour of which resembles that of coniine. The *hydrazone* melts at 182°, the *hydrazonesulphonic acid* at 283°, the *mercurochloride* at 173°, and the *ethiodide* at 192°. The *picrate* and *platinochloride* also crystallise well, and the *oxime* forms a white, crystalline powder. H. G. C.

Behaviour of "Dimethylpiperidine" and Allied Bases towards Hydrogen Chloride. By G. MERLING (*Annalen*, **264**, 310—351).—The tertiary base obtained by Hofmann (*Ber.*, **14**, 659) by the dry distillation of dimethylpiperidylammonium hydroxide, and named by him dimethylpiperidine, is an unsaturated compound of the constitution $CH_2\colon CH\cdot[CH_2]_3\cdot NMe_2$, and is termed by the author butallylcarbindimethylamine (methyl = carbin, methylamine = carbinamine). When this base is heated in a stream of hydrogen chloride, it is converted into methyl-α-methylpyrrolidine, and not into methylpiperidine, as was supposed by Hofmann. The experiments on which these statements are based, and others of a like nature, are described below.

Hydrochlorobutallylcarbindimethylamine, $CHClMe\cdot[CH_2]_3\cdot NMe_2$, is obtained in the form of its hydrochloride when Hofmann's "dimethylpiperidine" is heated in a stream of hydrogen chloride at 130—160°, and also when "dimethylpiperidine hydrochloride" is treated with an aqueous solution of hydrogen chloride saturated at 0°. This salt is a crystalline substance readily soluble in water; when melted in a stream of dry hydrogen, it gradually loses hydrogen chloride. The free *base* is a colourless oil. The *aurochloride*, $C_5H_{10}Cl\cdot NMe_2,HAuCl_4$, crystallises from hot concentrated hydrochloric acid in large, golden plates.

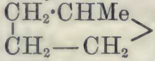
Dimethyl-α-methylpyrrolidylammonium chloride,



$$\begin{array}{l} CH_2\cdot CHMe \\ | \\ CH_2 - CH_2 \end{array} > NMe_2Cl,$$

is formed when hydrochlorobutallylcarbindimethylamine is heated at 150°, and the product freed from butallylcarbindimethylamine by heating it in a stream of hydrogen; it is a colourless, crystalline, deliquescent compound. The *platinochloride*, $(C_7H_{16}NCl)_2PtCl_4$, crystallises in orange-red octahedra, and is sparingly soluble in water.

The *aurochloride*, $C_7H_{16}NCl,AuCl_3$, is sparingly soluble in water, from which it crystallises in golden needles. The corresponding *ammonium iodide*, $C_7H_{16}NI$, prepared by treating methyl-α-methylpyrrolidine with methyl iodide in methyl alcoholic solution, crystallises from alcohol in small, colourless octahedra and cubes, turns yellow on exposure to light, and is very readily soluble in alcohol.

Methyl-α-methylpyrrolidine,  $\left.\begin{array}{l}CH_2\cdot CHMe\\ |\\ CH_2-CH_2\end{array}\right>NMe$, is formed with evolution of methyl chloride when the ammonium chloride just described is heated strongly; it is a colourless, basic oil, of sp. gr. 0·799 at 15°; it boils at 96—97°, is miscible with water, and has an odour of piperidine. The *platinochloride*, $(C_6H_{13}N)_2,H_2PtCl_6$, crystallises from hot water in flat, orange-yellow needles or prisms, and melts at about 225° with decomposition. The *aurochloride*, $C_6H_{13}N,HAuCl_4$, is sparingly soluble in cold water, and crystallises from hot water in golden needles melting at 215—217° with decomposition.

Butallylmethylcarbinamine, $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$, can be obtained by reducing the hydrazone of allylacetone with sodium amalgam in warm, alcoholic glacial acetic acid solution; it is a colourless, mobile liquid, having an odour of piperidine and a strong alkaline reaction; it is miscible with water, boils at 117—118°, and its sp. gr. is 0·779 at 15°. The *hydrochloride* and the *hydrobromide* are deliquescent, crystalline compounds. The *platinochloride*,

$$(C_6H_{13}N)_2,H_2PtCl_6,$$

crystallises in yellow needles and is moderately easily soluble in cold water; the *aurochloride* is a yellow, crystalline compound.

Butallylmethylcarbintrimethylammonium iodide,

$$CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

is obtained when the preceding compound is treated with methyl iodide and methyl alcoholic potash; it crystallises from alcohol in well-defined prisms, and melts at 199—200°. The corresponding *chloride*, prepared by treating the iodide with moist silver chloride, is a hygroscopic, crystalline compound.

Butallylmethylcarbindimethylamine, $CH_2{:}CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot NMe_2$, is formed, together with various other products, when the dry ammonium chloride just described is heated at 150—180° in a stream of air; it is a colourless oil of sp. gr. 0·780 at 15°, boils at 138—140°, and has a strong odour recalling that of piperidine. The *platinochloride*, $(C_6H_{11}NMe_2),H_2PtCl_6$, is an orange-yellow, crystalline substance readily soluble in water; the *aurochloride* is also crystalline.

Hydrochlorobutallylmethylcarbinamine hydrochloride,

$$CHMeCl\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2,HCl,$$

is formed when hydrogen chloride is passed into butallylmethylcarbinamine heated at 130°; it is a colourless, hygroscopic, crystalline substance. The *platinochloride*, $(C_6H_{14}NCl)_2,H_2PtCl_6$, is a pale-yellow, crystalline compound, and is decomposed by boiling water; the *aurochloride* is also crystalline, but the free *base* is a colourless oil. When hydrochlorobutallylmethylcarbinamine is heated on the water-bath, it is converted into $\alpha\alpha_1$-dimethylpyrrolidine hydrochloride, identical with the compound recently described by Tafel (Abstr., 1888, 1015; 1890, 1000). Dimethyl-$\alpha\alpha_1$-dimethylpyrrolidylammonium iodide crystallises in transparent cubes and octahedra, and decomposes at about 400°, but without melting (Tafel gives 255—256° as the melting point of this compound).

Hydrochlorobutallylmethylcarbindimethylamine hydrochloride,

$$CHMeCl\cdot CH_2\cdot CH_2\cdot CHMe\cdot NMe_2,HCl,$$

prepared by passing hydrogen chloride into butallylmethylcarbindimethylamine heated at 130°, is a colourless, hygroscopic, crystalline substance. The *platinochloride*, $(C_6H_{12}Cl\cdot NMe_2)_2,H_2PtCl_6$, is a yellow, crystalline compound; it melts at 91—93°, and is decomposed by boiling water. The *aurochloride* is a yellow powder melting at 76—77°. The free *base* is a colourless oil which, when heated on the water-bath, is readily converted into *dimethyl-$\alpha\alpha_1$-dimethylpyrrolidylammonium chloride;* on further heating, methyl chloride is evolved and methyl-$\alpha\alpha_1$-dimethylpyrrolidine, identical with Tafel's trimethylpyrrolidine (*loc. cit.*) is formed.

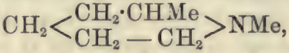
Dimethyl-α-pipecolylammonium iodide, $C_8H_{18}NI$, is formed when α-pipecoline, prepared by Ladenburg's method, is treated with methyl iodide and potash in methyl alcoholic solution; it crystallises from hot alcohol in long, white crystals, and is sparingly soluble in cold alcohol.

Pentallylcarbindimethylamine, $CH_2{:}CH\cdot[CH_2]_4\cdot NMe_2$, is obtained when the ammonium iodide just described is treated with moist silver oxide, and the hydroxide thus formed gradually heated to 140°; it is a colourless oil, of sp. gr. 0·767 at 15°, boils at 143—143·5°, and has an odour of piperidine; it has a strongly alkaline reaction, and is not miscible with water. The *platinochloride* is an oil, and the *aurochloride* an unstable, crystalline compound.

Hydrochloropentallylcarbindimethylamine hydrochloride,

$$CHClMe\cdot[CH_2]_4\cdot NMe_2,HCl,$$

can be obtained by passing hydrogen chloride into pentallylcarbindimethylamine heated at 160°; it is a very hygroscopic, crystalline substance. The *platinochloride* and the *aurochloride* are oils.

Methyl-α-pipecoline,  $CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2 - CH_2\end{matrix}>NMe$, is formed when the preceding compound is decomposed with soda, the colourless, oily base thus obtained heated first at 120° to convert it into dimethyl-α-pipecolylammonium chloride, and then at a higher temperature to eliminate methyl chloride; it can also be obtained by heating dimethyl-α-pipecolylammonium chloride prepared directly from α-pipecoline. It is a colourless oil, of sp. gr. 0·826 at 15°, boils at 126—128°, and is not miscible with water. The *platinochloride*, $(C_7H_{15}N)_2,H_2PtCl_6$, separates from hot water in compact, orange-red crystals melting at 180—185°.

Pentallylcarbintrimethylammonium iodide, $CH_2{:}CH\cdot[CH_2]_4\cdot NMe_3I$, is formed when pentallylcarbindimethylamine is treated with methyl iodide in methyl alcoholic solution; it separates from alcoholic ether in colourless plates melting at 126—129°; when treated with moist silver oxide, it is converted into a strongly alkaline hydroxide, which is decomposed, on heating at about 160°, into water, trimethylamine, diallyl (b. p. 60—61°), and a hydrocarbon (b. p. 80—83°) isomeric with diallyl.

The *hydrocarbon*, boiling at 80—83°, is a colourless, refractive oil, of sp. gr. 0·727 at 15°, and has an odour like that of diallyl; it combines readily with bromine, yielding a *tetrabromide* $C_6H_{10}Br_4$, which crystallises from hot glacial acetic acid in lustrous plates melting at 160—162°; on oxidation with chromic acid, it yields carbonic anhydride and acetic acid.

When butallylmethylcarbintrimethylammonium iodide (m. p. 199—200°) is digested with moist silver oxide, it is converted into the corresponding hydroxide; this substance decomposes at about 160° into water, trimethylamine, diallyl, and a hydrocarbon (b. p. 80—83°) identical with that obtained from pentallylcarbintrimethylammonium iodide in like manner.

F. S. K.

Formation of Bases of the Quinoline Series. By E. LELLMANN and W. LIPPERT (*Ber.*, **24**, 2623—2624).—It is known that either aniline or nitrobenzene yields quinoline when heated with glycerol and sulphuric acid, and that in the one case oxidation, in the second reduction, must occur. Azobenzene occupies an intermediate position between aniline and nitrobenzene, and, if found to react with acraldehyde, might, therefore, be expected to do so without either oxidation or reduction being necessary. This conclusion is confirmed by experiment, since the authors find that azobenzene (compare Claus and Stegelitz, Abstr., 1887, 173) and its derivatives yield bases of the quinoline series when heated with glycerol and sulphuric acid. Azobenzene and parazotoluene give, respectively, quinoline and toluquinoline, whilst amidoazobenzene forms a mixture of quinoline and pseudophenanthroline. The yield in each case was small.

W. P. W.

Preparation of Amidoquinoline. By J. EPHRAIM (*Ber.*, **24**, 2817—2820).—*α-Phenylhydrazoquinoline*, $C_9NH_6{\cdot}NH{\cdot}NHPh$, is prepared by carefully heating a mixture of α-chloroquinoline (1 mol.) and phenylhydrazine (2 mols.) in a reflux apparatus, over a free flame, extracting the uncombined portion of the reagents, and the phenylhydrazine hydrochloride produced, with boiling water, and crystallising from absolute alcohol. It then separates in white needles, melts at 191° with decomposition, and is readily soluble in glacial acetic acid and chloroform, almost insoluble in ether; it gives a violet colour with concentrated sulphuric acid, which, on diluting with water, becomes rose-coloured. The yield is equal to that of the chloroquinoline employed.

α-Phenylazoquinoline, $C_9NH_6{\cdot}N_2Ph$, is formed by oxidising the hydrazo-compound, best as follows:—The hydrazo-derivative is dissolved in glacial acetic acid, an excess of ferric chloride added, and after a while the mixture diluted with water, when the azo-derivative separates in delicate, red needles; it melts at 93°, and is readily soluble in glacial acetic acid, alcohol, and ether; it exhibits the same colour reaction with concentrated sulphuric acid as the hydrazo-derivative.

α-Amidoquinoline, $C_9NH_6{\cdot}NH_2$ [$NH_2 = 2'$], is obtained by heating α-phenylhydrazoquinoline (1 gram) with hydriodic acid (1·7 grams) and amorphous phosphorus (0·5 gram) in a sealed tube at 180° for an hour, rendering the product alkaline, driving over the aniline with a current of steam, and extracting the residual solution with ether, from which the new base is obtained as a violet, crystalline mass, which, when crystallised from light petroleum, melts at 114°, and is readily soluble in alcohol, ether, chloroform, and benzene; the *picrate* and the *platinochloride* are sparingly soluble compounds. A *hydrazo-derivative* melting at 197° is obtained from α-chlorolepidine.

A. R. L.

Tetrahydro-derivatives of β-Naphthaquinoline and β-Naphthaquinaldine. By E. BAMBERGER and R. MÜLLER (*Ber.*, **24**, 2641—2647).—β-Naphthaquinoline (Skraup and Cobenzl, Abstr., 1883, 1010) is most readily purified by pouring the product of the Skraup reaction into water, neutralising partially with caustic soda, filtering from tarry matters, and, with the object of removing all resinous matters from solution, heating the filtrate on a water-bath with sodium nitrite until it gives the reactions of nitrous acid. The pure base separates in the solid form on the addition of excess of alkali to the filtrate. It boils at 349·5—350° (thermometer in vapour) under 721 mm. pressure.

Tetrahydro-β-naphthaquinoline, $C_{13}H_{13}N$, is obtained when β-naphthaquinoline (20 grams), dissolved in concentrated hydrochloric acid, is gradually added to a boiling mixture of tin (80 grams) and hydrochloric acid (500 grams), and heated until the metal is dissolved. The crystalline stannochloride, which separates on cooling, is decomposed by aqueous soda, and the base purified by distillation with steam and subsequent crystallisation from light petroleum. It crystallises in lustrous, silvery-white needles or scales, melts at 93·5°, and dissolves readily in the ordinary organic solvents, but only sparingly in water. The solutions in indifferent solvents are destitute of fluorescence, but those in mineral acids show a beautiful blue fluorescence, resembling that of anthracene. Ferric chloride or potassium dichromate, added to the acid solution, produces a deep, reddish-brown coloration, rapidly changing to dark brown. The *hydrochloride*, $C_{13}NH_{13},HCl$, crystallises in silvery-white prisms, melts at 230·5—231°, and dissolves easily in water, but only sparingly in strong hydrochloric acid; the *sulphate* forms lustrous, white needles, and is very soluble in water. The *acetyl* derivative, $C_{13}H_{12}NAc$ [$Ac = 1''$], crystallises in white prisms, melts at 77°, and is sparingly soluble in water, but readily in most other solvents. The *nitroso*-derivative, $C_{13}NH_{12}{\cdot}NO$, crystallises from alcohol in silvery-white prisms or scales, melts at 105·5°, and dissolves easily in benzene, chloroform, ether, &c.

1″-Benzeneazotetrahydro-β-naphthaquinoline, $C_{13}NH_{12}{\cdot}N_2Ph$ [$N_2Ph = 1''$], prepared by the action of diazobenzene chloride on tetrahydro-β-naphthaquinoline in the presence of sodium acetate, crystallises from light petroleum in yellow needles of golden lustre, melts at 96·5—97°, and dissolves easily in the ordinary organic solvents.

When warmed with mineral acids, it decomposes into the tetrahydro-base, phenol, and nitrogen.

Tetrahydro-β-naphthaquinaldine is obtained by reducing β-naphthaquinaldine by the method just described. It crystallises from light petroleum in hard, thick, glassy prisms, melts at 51·5—52°, dissolves readily in the ordinary organic solvents, but only sparingly in water, forming fluorescent solutions which lose their blue fluorescence on the addition of a mineral acid. Ferric chloride or potassium dichromate added to an acid solution produces a reddish-brown coloration, which becomes brighter and eventually greenish-yellow when the mixture is warmed. The *hydrochloride*, $C_{14}NH_{15},HCl$, crystallises in white prisms, melts at 239—240°, and is readily soluble in water, but sparingly in hydrochloric acid. The *acetyl* derivative, $C_{14}H_{14}NAc$, forms white needles, melts at 86—86·5°, and dissolves easily in organic solvents. The *nitroso*-derivative, $C_{14}NH_{14}\cdot NO$ [NO = 1″], crystallises from alcohol in straw-yellow, lustrous scales, and melts at 69—69·5°. The *benzeneazo*-compound has not yet been obtained in crystalline form.

W. P. W.

Octohydro-derivatives of β-Naphthaquinoline. By E. BAMBERGER and R. MÜLLER (*Ber.*, **24**, 2648—2661).—The first part of this paper is devoted to a restatement of the effect of reduction on the properties of β-naphthaquinoline, for which a previous paper may be consulted (Abstr., 1890, 1303). When β-naphthaquinoline (10 grams) is reduced with sodium (30 grams) and amyl alcohol (250 grams) in the usual way, a mixture of the "alicyclic" and "aromatic" octohydrides is obtained. The relative proportion of the two bases varies slightly in different experiments, but the "aromatic" derivative is always the chief product, the average yield of the "alicyclic" base being about 3 per cent. of the naphthaquinoline employed. To separate the bases, the fluorescent amyl alcohol layer is acidified, the alcohol removed by steam distillation, the residue rendered alkaline, and the bases distilled with steam. The solid distillate is extracted with light petroleum to free it from a very small quantity of a third base insoluble in that solvent, and the "alicyclic" constituent separated as carbonate by treating the filtrate with moist carbonic anhydride. The carbonate is freed from small quantities of the "aromatic" base, which adhere to it even after washing with light petroleum, either by repeating the precipitation with carbonic anhydride several times, or by adding nitrous acid to the cold dilute aqueous solution and extracting the resulting "aromatic" nitrosamine with ether.

ac.-Octohydro-β-naphthaquinoline, $C_{13}NH_{17}$, crystallises from dilute aqueous soda in long, silky, matted needles, or from alcohol in long, glassy prisms, melts at 91°, boils at 321° under 727 mm. pressure, has a basic odour, and is volatile with steam. It gives no colour reactions with ferric chloride, potassium dichromate, or diazotised bases, and in its properties resembles the "alicyclic" tetrahydronaphthylamines; its physiological action, for example, being, according to Filehne, very similar to that of those bases (compare Abstr., 1889, 737), and in no sense like that of quinoline. The *hydrochloride*, $C_{13}NH_{17},HCl$, crystallises in thick, glassy, monoclinic prisms, melts at 252°, and is readily soluble in water and alcohol, but only sparingly in hydrochloric acid; the *platinochloride* crystallises in golden-yellow, serrated, thin prisms, melts at 250° with blackening, and dissolves very sparingly in cold water; the *nitrate* forms lustrous prisms, somewhat sparingly soluble in cold water; the *nitrite* crystallises from water in short, thick, glassy prisms, melts at 238°, and is not decomposed by boiling water or cold mineral acids. The *acetyl* derivative, $C_{13}H_{16}NAc$, crystallises from light petroleum in strongly refractive, glassy prisms, from water in small needles, and dissolves readily in the ordinary solvents. The *benzeneazo*-compound, $C_{13}NH_{16}\cdot N_2Ph$ [$N_2Ph = 1''$], obtained by the action of diazobenzene chloride on the base in the presence of sodium acetate, crystallises from aqueous alcohol in silvery-white, flat needles, melts at 95°, is readily soluble in the ordinary organic solvents, and yields a *picrate*, $C_{19}H_{21}N_3,C_6H_2(NO_2)_3\cdot OH$, crystallising in lustrous, golden-yellow needles. The *nitroso*-derivative, $C_{13}NH_{16}\cdot NO$, prepared by heating a solution of the base in excess of acid with the calculated quantity of sodium nitrite at 110—120° for 5 hours, crystallises from alcohol in lustrous, flat, serrated, silvery-white prisms, melts at 122·5°, and dissolves readily in ether, chloroform, benzene, and boiling alcohol.

ar.-Octohydro-β-naphthaquinoline, $C_{13}NH_{13}$, exhibits a remarkable power of crystallisation. From its solution in light petroleum, it usually separates in large, transparent, colourless prisms, whose length seems to be conditioned only by the size of the containing vessel. If, however, the concentrated solution is slowly cooled, it forms pale yellow, shorter prisms an inch in thickness, belonging either to the monoclinic, or more probably, the triclinic system; exact crystallographic measurements could not be made, since the crystals, on removal from the solvent, became white and opaque in a few seconds, owing to volatilisation of the light petroleum crystallised with the base. The mother liquor of these efflorescent crystals solidifies after a few minutes to a mass of long, thin, silky needles, which do not alter on exposure to the air. The base melts at 60·5°, boils at 325° under 727 mm. pressure, has a neutral reaction, and dissolves easily in organic solvents, but only sparingly in water. In its reactions, it resembles the "aromatic" tetrahydronaphthylamines; thus it reduces alcoholic silver nitrate in the cold and platinic chloride on warming, reacts with diazotised sulphanilic acid forming a dark claret colouring matter, and gives a yellowish coloration on warming its acid solution with ferric chloride or potassium dichromate. The *hydrochloride*, $C_{13}NH_{17},HCl$, crystallises either in silvery-white scales or long, glassy prisms, melts at 219°, and is soluble in alcohol and chloroform. The *platinochloride*, $(C_{13}NH_{17})_2,H_2PtCl_6 + 2H_2O$, forms bright-yellow, lustrous scales, melts at 178°, and on warming becomes black, owing to the separation of platinum. The *acetyl* derivative, $C_{13}NH_{16}\cdot Ac$, crystallises in scales or flat, silvery-white prisms, melts at 68·5—69°, and dissolves readily in most solvents, but only sparingly in water. The *nitroso*-derivative, $C_{13}NH_{16}\cdot NO$ [$NO = 1''$], crystallises by very slow evaporation of its alcoholic solution in short, thick, glassy, monoclinic prisms, $a : b : c = 2{\cdot}4245 : 1 : 2{\cdot}75495$; $\beta = 85°$, observed forms $0P$, $\infty\bar{P}\infty$, $-P$, $+P$, and $+2\bar{P}\infty$. It melts at 106°.

W. P. W.

Octohydro-derivatives of β-Naphthaquinaldine. By E. BAMBERGER and L. STRASSER (*Ber.*, **24**, 2662—2669).—β-Naphthaquinaldine (12 grams), on reduction with sodium (32 grams) and boiling amyl alcohol (350 grams), yields a mixture of an "aromatic" octohydro-β-naphthaquinaldine with a very small quantity of "alicyclic" octohydro-β-naphthaquinaldine. These bases can be separated by the method described in the preceding abstract.

ar.-Octohydro-β-naphthaquinaldine, $C_{14}NH_{19}$, crystallises from light petroleum in colourless, glassy prisms, from dilute alcohol in glistening scales, melts at 75°, volatilises slowly with steam, and dissolves readily in alcohol, benzene, chloroform, &c., but only sparingly in water. It exhibits reducing properties, and on the addition of silver nitrate to its alcoholic solution, gives first a blue colour and then a separation of metallic silver. Ferric chloride added to the warm aqueous solution of its hydrochloride produces a yellow colour which eventually changes to reddish-brown, with the separation of reddish-brown flocks. The *hydrochloride*, $C_{14}NH_{19},HCl$, crystallises in white, lustrous, feathery crystals, melts at 210°, and dissolves readily in alcohol, but only sparingly in hydrochloric acid. On the addition of platinic chloride to its aqueous solution, yellow needles of a platinochloride are obtained, which become black on heating the solution, owing to a separation of platinum. The *nitrate*, $C_{14}NH_{19},HNO_3$, crystallises in lustrous, white needles, melts at 170°, and is easily soluble in water and dilute nitric acid on boiling, but only sparingly in the cold. The *acetyl* derivative, $C_{14}NH_{18}Ac$ $[Ac = 1'']$, crystallises from light petroleum in aggregates of lustrous needles, melts at 92°, and dissolves readily in most solvents, but only sparingly in water. The *nitroso*-derivative, $C_{14}NH_{18}{\cdot}NO$, forms straw-yellow, lustrous needles, melts at 86°, and is easily soluble in ether, benzene, chloroform, and boiling alcohol.

$1''$-*Benzeneazo-ar.-octohydro-β-naphthaquinaldine*, $C_{14}NH_{18}{\cdot}N_2Ph$ $[N_2Ph = 1'']$, is obtained when a solution of octohydro-β-naphthaquinaldine and sodium acetate in aqueous alcohol is treated with the calculated quantity of diazobenzene chloride. By slow evaporation of its solution in light petroleum, it crystallises in pale-yellow, glassy, thick, rhombic prisms, $a : b : c = 0{\cdot}8037 : 1 : 0{\cdot}5600$, forms observed $2\breve{P}\infty$ and P, melts at 97·5—98°, and is extremely soluble in ether, chloroform, and benzene. When boiled with mineral acids, it decomposes in the normal way into octohydro-β-naphthaquinoline, phenol, and nitrogen; as anticipated, however, it does not undergo intramolecular change into the azo-compound on treatment of its alcoholic solution with hydrochloric acid, since the para-position is not open in the central ring, which by hydrogenation of the lateral rings has acquired properties identical with those of benzene.

$2'$-*Benzeneazo-ar.-octohydro-β-naphthaquinaldine*, $C_{14}NH_{18}{\cdot}N_2Ph$ $[N_2Ph = 2']$, is formed when a cooled dilute alcoholic solution of the hydrochloride of the base is treated with diazobenzene nitrate. It crystallises from alcohol in dark, ruby-red prisms of greenish, bronze-like lustre, and dissolves readily in alcohol, ether, chloroform, &c., but only sparingly in water. The alcoholic solution is raspberry-red in colour, but, on the addition of a drop of concentrated hydrochloric acid, becomes emerald-green. Concentrated sulphuric acid dissolves it, forming a raspberry-red solution, which, on adding a little water, becomes emerald-green, and on further dilution, becomes rose-coloured and seemingly fluorescent, owing to the precipitation of the colouring matter. *Sulphobenzeneazo-ar.-octohydro-β-naphthaquinoline* is a greenish-black, crystalline powder which dissolves in alcohol and water with a deep-red colour, and in alkalis forming dark claret solutions.

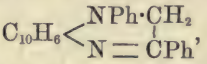
Orthamido-ar.-octohydro-β-naphthaquinaldine [$NH_2 = 2'$] is prepared by boiling the alkaline solution of the sulphobenzeneazo-derivative with zinc dust until the colour becomes bright-yellow, and subsequently extracting with ether. It exhibits the reactions of an orthodiamido-derivative of benzene on treatment with dilute solutions of ferric chloride or potassium dichromate, and on boiling with acetic acid is converted into *α-methyl-ar.-octohydro-β-naphthaquinaldimidazole.* The imidazole hydrochloride crystallises from alcohol or ether-alcohol in glassy prisms, melts at 262° with decomposition, dissolves readily in acids, and gives no colour reactions with ferric chloride or potassium dichromate.

ac.-Octohydro-β-naphthaquinaldine, $C_{14}NH_{19}$, crystallises in long, silky needles, dissolves easily in the ordinary organic solvents, but only sparingly in water, has a strongly alkaline reaction, and volatilises readily with steam. It is destitute of reducing powers, and exhibits the properties of an "alicyclic" base. The *hydrochloride* crystallises in silvery scales, and dissolves readily in water, but only sparingly in hydrochloric acid; the *platinochloride* forms orange-red, flat needles.

W. P. W.

A New Class of Fluorescent Colouring Matters of the Quinoxaline Series. By O. FISCHER and M. BUSCH (*Ber.*, **24**, 2679—2683). —An azonium base identical with the compound (m. p. 167°) obtained by oxidising triphenyletho-αβ-hydronaphthaquinoxaline (this vol., p. 1109) is formed when benzile is treated with phenylorthonaphthylenediamine as described by Witt (Abstr., 1887, 729).

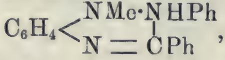
1 : 3-*Diphenyletho-αβ-dihydronaphthaquinoxaline*,



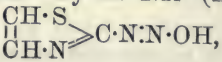
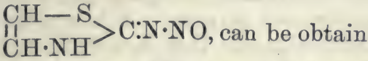
$$C_{10}H_6 < \begin{matrix} NPh\cdot CH_2 \\ N = CPh \end{matrix},$$

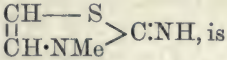
is formed, together with a very small quantity of a dark-red substance described below, when benzoylcarbinol, prepared by hydrolysing acetylacetophenone with barium carbonate, is heated with phenylorthonaphthylenediamine at 150—160° in sealed tubes for 4—5 hours. The crude product is dissolved in a mixture of benzene (1 part) and alcohol (3 parts), from which, on keeping for a long time, the quinoxaline is deposited in compact, orange-red needles. It melts at 164—165°, and is readily soluble in benzene, but more sparingly in ether and glacial acetic acid, very sparingly in alcohol, and almost insoluble in light petroleum; its solutions show an intense yellowish-green fluorescence. It dissolves in concentrated sulphuric acid and in concentrated hydrochloric acid, yielding a dark brownish-red solution, from which it is reprecipitated in a yellow, flocculent condition on the addition of water. On oxidation with ferric chloride, it is converted almost quantitatively into diphenylethonaphthazonium hydroxide, identical with the compound previously described (*loc. cit.*).

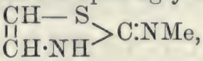
The dark-red bye-product mentioned above is obtained in crystals when the alcoholic benzene mother liquors from the quinoxaline base are mixed with ether and then slowly evaporated; it is soluble in benzene and ether, but only sparingly in alcohol and light petroleum, its solutions showing a beautiful purple-red fluorescence; it melts at about 194—196°, and forms a stable salt with sulphuric acid.

n-Methyldiphenyldihydroquinoxaline,  $C_6H_4{<}\begin{matrix}NMe\cdot NHPh\\ N = CPh\end{matrix}$, is formed when benzoïn is heated with methylorthophenylenediamine at 160—170° for 5—6 hours; it crystallises from alcohol in concentrically-grouped, yellow needles, melts at 133°, and is readily soluble in benzene and ether, but only moderately easily in alcohol, and very sparingly in light petroleum; its solutions show a greenish-yellow fluorescence. It is a feeble base, its salts being partially decomposed by water; it dissolves in concentrated sulphuric acid, yielding a yellow solution, which first changes to red and then becomes yellow again on the addition of water. When the quinoxaline is heated with ferric chloride and hydrochloric acid in alcoholic solution, it is converted into an ammonium base, the ferrichloride of which crystallises in long, yellow prisms.

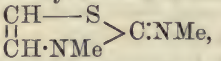
F. S. K.

Nitroso-derivatives of the Thiazoles. By E. NÄF (*Annalen*, **265**, 108—128).—*Diazothiazole hydrate*,  $\begin{matrix}CH\cdot S\\ \| \\ CH\cdot N\end{matrix}{>}C\cdot N{:}N\cdot OH$, or *μ-nitrosoimidothiazoline*,  $\begin{matrix}CH - S\\ \| \\ CH\cdot NH\end{matrix}{>}C{:}N\cdot NO$, can be obtained in a slightly impure condition, by gradually adding a well-cooled, concentrated solution of sodium nitrite to a concentrated aqueous solution of amidothiazole nitrate cooled to −10°; the amorphous, orange-red, flocculent precipitate is quickly separated by filtration at a low temperature and dried in a desiccator. It is very unstable when moist, and even in the dry state it gradually turns black; when quickly heated, it decomposes at about 140° with explosion. It is soluble in alcohol and ether, but insoluble in water; its conversion into chloro- and bromo-thiazole has been previously described by Schatzmann (this vol., p. 744).

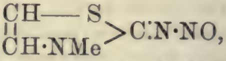
μ-Imido-n-methylthiazoline,  $\begin{matrix}CH — S\\ \| \\ CH\cdot NMe\end{matrix}{>}C{:}NH$, is formed when amidothiazole is heated with methyl iodide in methyl alcoholic solution at 130° for several hours, and the hydriodide obtained in this way decomposed with potash; it is a yellowish-brown, very hygroscopic, strongly alkaline liquid. The *hydriodide*, $C_4H_6N_2S,HI$, crystallises in colourless plates, and melts at 175°. The *hydrochloride* crystallises from water, in which it is very readily soluble, in large plates, and melts at 97°; the *platinochloride* is sparingly soluble.

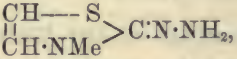
μ-Methylimidothiazoline,  $\begin{matrix}CH — S\\ \| \\ CH\cdot NH\end{matrix}{>}C{:}NMe$, is produced when an

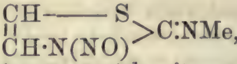
aqueous solution of methylthiocarbamide is warmed with dichlorether; it is a yellowish-brown oil, which, on keeping, gradually solidifies to a mass of very hygroscopic crystals. The *hydrochloride*, $C_4H_6N_2S,HCl$, is a semi-crystalline, hygroscopic compound melting at 79—80°. The *platinochloride* crystallises in long needles.

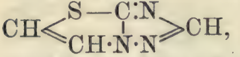
Dimethylimidothiazoline,  $\left.\begin{array}{l}\mathrm{CH{-}{-}S}\\ \|\\ \mathrm{CH{\cdot}NMe}\end{array}\right>\mathrm{C{:}NMe}$, can be obtained by methylating either of the bases just described, but more conveniently by warming an aqueous solution of dimethylthiocarbamide with dichlorether; it is a hygroscopic liquid.

The *hydrochloride*, $C_5H_8N_2S,HCl$, crystallises well, and melts at 222°.

μ-Nitroso-n-methylimidothiazoline,  $\left.\begin{array}{l}\mathrm{CH{-}{-}S}\\ \|\\ \mathrm{CH{\cdot}NMe}\end{array}\right>\mathrm{C{:}N{\cdot}NO}$, is precipitated in yellow, lustrous plates when a concentrated solution of sodium nitrite is added to a solution of μ-imidomethylthiazoline hydrochloride in well-cooled, very dilute hydrochloric acid; it melts at 161° with a slight explosion, and is soluble in alcohol and ether, but only sparingly in water. The dry compound is stable, and dissolves unchanged in alkalis, but when treated with concentrated mineral acids, or with powerful reducing agents, it is reconverted into μ-imidomethylthiazoline.

n-Methylthiazolinehydrazine,  $\left.\begin{array}{l}\mathrm{CH{-}{-}S}\\ \|\\ \mathrm{CH{\cdot}NMe}\end{array}\right>\mathrm{C{:}N{\cdot}NH_2}$, is formed in small quantities when an alcoholic solution of the preceding compound is mixed with excess of zinc-dust, and acetic acid gradually added to the well-cooled mixture; it is a yellow, disagreeably smelling oil. The *hydrochloride*, $C_4H_7N_3S,HCl$, and the sparingly soluble *picrate* crystallise in yellow needles.

n-Nitroso-μ-methylimidothiazoline,  $\left.\begin{array}{l}\mathrm{CH{-}{-}{-}S}\\ \|\\ \mathrm{CH{\cdot}N(NO)}\end{array}\right>\mathrm{C{:}NMe}$, can be obtained by treating μ-methylimidothiazoline with nitrous acid under the conditions given above; it forms small, yellowish crystals, has a characteristic odour recalling that of acetamide, and is much more unstable than the isomeride described above, being converted into resinous products on keeping in a dry condition, or on boiling with water or alcohol. It turns black when slowly heated, and melts at about 140°, but when heated quickly it explodes at about 110—120°; it is freely soluble in alkalis and in ammonia, by which it is completely decomposed. The corresponding hydrazine could not be obtained.

The hydrochloride of a base which the author names *thiazoletriazole*,  $\mathrm{CH}\left<\begin{array}{c}\mathrm{S{-}C{:}N}\\ |\\ \mathrm{CH{\cdot}N{\cdot}N}\end{array}\right>\mathrm{CH}$, is formed when freshly prepared *n*-nitroso-μ-methylimidothiazoline is dissolved in well-cooled 10 per cent. hydrochloric acid, and the solution warmed until no further evolution of gas takes place; on keeping for some time, the *hydrochloride*,

$$C_4H_3N_3S,HCl + 2H_2O,$$

is deposited in needles, which turn brown and lose their water at 130—140°. and melt at 210—220°. The *hydrobromide*,

$$C_4H_3N_3S,HBr + 2H_2O,$$

forms long, prismatic crystals, turns brown on keeping, loses its water at 130—140°, and decomposes completely at a higher temperature, but without melting. The free *base* is a brown oil, which gradually solidifies to a vitreous mass; it is very readily soluble in water, has an alkaline reaction, and reduces Fehling's solution; when its hydrochloride is treated with sodium nitrite in aqueous solution, a large quantity of *n*-nitroso-*μ*-methylimidothiazoline is formed.

μ-Phenylimidothiazoline, $C_9H_8N_2S$, prepared by treating dichlorether with phenylthiocarbamide and decomposing with potash the salt produced, crystallises from alcohol, ether, and benzene in small, colourless needles, and melts at 124°; its salts are not easily obtained in crystals.

Diphenylimidothiazoline, $C_{15}H_{12}N_2S$, obtained from diphenylcarbamide in like manner, is a granular, crystalline substance melting at 105°.

μ-Phenyl-n-nitrosoimidothiazoline, $C_9H_7N_3SO$, is precipitated in the form of a microscopic, crystalline powder on treating *μ*-phenylimidothiazoline with sodium nitrite in well-cooled, dilute hydrochloric acid solution; it forms yellow crystals, melts at 58°, and decomposes on keeping. It is insoluble in alkalis, and, when treated with acids, it is reconverted into *μ*-phenylimidothiazoline. F. S. K.

Action of Hydriodic Acid on Quinine and Cinchonine. By E. LIPPMANN and F. FLEISSNER (*Ber.*, **24**, 2827—2829).—The action of hydriodic acid on quinine is similar to that of hydrochloric or hydrobromic acid on the base (*Monatsh.*, **12**), and leads to the formation of hydriodoquinine hydriodide, $C_{20}H_{24}N_2O_2,3HI$, which, on treatment with ammonia, yielded hydriodoquinine, $C_{20}H_{24}N_2O_2HI$, with the elimination of 2 mols. of hydrogen iodide. When boiled with alcoholic potash, hydriodoquinine is converted into isoquinine. A better yield of this base is obtained by heating hydriodoquinine hydriodide with water at 150—160° for about six hours, adding the pale-yellow solution to aqueous ammonia, extracting with ether, and drying the ethereal solution over caustic potash. After a short time, the sparingly soluble isoquinine crystallises from the solution, and a further quantity can be obtained by evaporation, the ethereal mother liquor containing quinine.

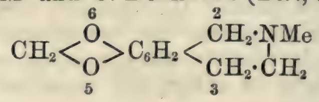
Hydriodocinchonine hydriodide, $C_{19}H_{22}N_2O,3HI$, is formed when cinchonine, free from sulphuric acid, is slowly stirred into warm hydriodic acid (sp. gr. 1·7—1·8), and can be freed from cinchonine hydriodide by washing the crystalline precipitate with alcohol. It crystallises in small, bright-yellow, lustrous prisms, decomposes when heated at 215°, and dissolves sparingly in alcohol and cold water, but easily in hot water. On digestion with warm, dilute aqueous ammonia, it is converted into *hydriodocinchonine*, $C_{19}H_{22}N_2OHI$, which crystallises in slender, silky needles, melts at 158—160°, dissolves very sparingly in ether, but more easily in alcohol, and yields a *platinochloride* of the composition $C_{19}H_{22}N_2OHI + H_2PtCl_6$. Cinchonine is regenerated when hydriodocinchonine hydriodide is heated with water under pressure. W. P. W.

Quinethyline. By E. GRIMAUX and A. ARNAUD (*Compt. rend.*, **112**, 1364—1367).—It has been shown in a former communication that quinine is a methyl ether of cupreïne; quinethyline is the corresponding ethyl ether. It is prepared from specially purified cupreïne as follows:—A molecular proportion of dry cupreïne is dissolved in alcohol, to which has been added 1½ mols. of sodium, and heated in sealed tubes, at 95—100° with 1½ mols. of ethyl nitrate for from 12 to 15 hours. The alcohol is distilled off, the residue taken up with acidified water, an excess of soda added, and the new base extracted with ether. The ethereal solution is then shaken with dilute sulphuric acid, the aqueous solution separated from the ether, heated on the water-bath, and carefully neutralised by ammonia. When the concentrated liquor is cooled, strongly coloured basic sulphate of the base separates. The crude product is converted into the normal sulphate, which is purified by heating with animal charcoal and subsequently recrystallising it from boiling water. The base is precipitated from a cold, concentrated solution of the normal sulphate by the addition of a slight excess of ammonia. The precipitate is white and amorphous, much resembling quinine; it consists of hydrates melting at 60°.

The dry, pulverulent base may be obtained by desiccating in dry air, and afterwards heating at 100—120°; it melts at 160°. It is very soluble in all the ordinary solvents for alkaloïds, and yields very fluorescent solutions with excess of sulphuric acid. It does not crystallise from alcohol, behaving in exactly the same way as quinine. Large, colourless, transparent crystals of a hydrate may easily be obtained. The base is lævorotatory; its solution in absolute alcohol gives $[\alpha]_D = -169{\cdot}4°$.

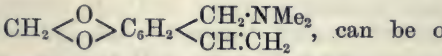
The *normal sulphate*, $C_{21}H_{26}N_2O_2,SO_4H_2 + 8H_2O$, crystallises in large, colourless, eight-sided prisms, efflorescing rapidly in the air. It dissolves in 51·1 parts of water at 19°, and is very soluble in boiling water. When heated with the calculated quantities of hydriodic acid and iodine in alcoholic solution, it yields small, garnet-red needles differing from the plates of herapathite given by quinine.

The *basic sulphate*, $(C_{21}H_{26}N_2O_2)_2,SO_4H_2 + H_2O$, is readily prepared from the normal sulphate by dissolving the latter in boiling water and neutralising exactly with dilute ammonia, using litmus as indicator. It forms crystalline plates of a silky lustre, requiring 397 parts of water for solution at 15°. Its solution in dilute hydrochloric acid gives $[\alpha]_D = -233{\cdot}1°$. The yield of pure basic sulphate was about 35 parts per 100 of cupreïne taken. W. T.

Hydrastine. By M. FREUND and C. DORMEYER (*Ber.*, **24**, 2730—2741).—Hydrohydrastinine,  $CH_2{<}\begin{smallmatrix}\overset{6}{O}\\ \underset{5}{O}\end{smallmatrix}{>}C_6H_2{<}\begin{smallmatrix}\overset{2}{CH_2}\cdot NMe\\ \vert\\ \underset{3}{CH_2}\cdot CH_2\end{smallmatrix}$ (compare

Freund and Will, Abstr., 1887, 383), is best prepared by reducing hydrastinine with 8 per cent. sodium amalgam in dilute sulphuric acid solution; the yield of crystalline product is 90 per cent. of the base employed.

Hydrohydrastinine methiodide, $C_{11}H_{13}NO_2,MeI$, is deposited in colourless crystals when a slight excess of the theoretical quantity of methyl iodide is added to a methyl alcoholic solution of hydrohydrastinine, and the mixture kept for some time; it crystallises from hot water in needles, and from dilute alcohol in iridescent plates, melts at 227—228°, and is not acted on by boiling, concentrated potash, or when melted with potash. The *platinochloride*, $(C_{12}H_{16}NO_2Cl)_2,PtCl_4$, is formed when an aqueous solution of the methiodide is digested with silver chloride, and the filtrate treated with platinic chloride; it crystallises from hot water in well-defined needles, and melts at 230°.



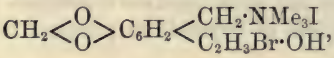
Methylhydrohydrastinine, $CH_2<\substack{O\\O}>C_6H_2<\substack{CH_2\cdot NMe_2\\CH:CH_2}$, can be obtained by digesting an aqueous solution of the methiodide just described with silver chloride, and decomposing the product with boiling, concentrated potash; it is an almost colourless, moderately mobile oil, having an amine-like odour, and strong basic properties; it is soluble in ether, alcohol, and carbon bisulphide, and cannot be distilled. The *hydriodide*, $C_{12}H_{15}NO_2,HI$, is easily obtained by dissolving the base in dilute hydrochloric acid, and adding potassium iodide to the solution; it crystallises from hot water in colourless, lustrous, hexagonal prisms, melts at 220—221°, and is decomposed by potash. On adding potassium dichromate to a dilute solution of the hydriodide, a golden-yellow substance is precipitated in needles which melt at 150° with decomposition. The *platinochloride*,

$$(C_{12}H_{15}NO_2)_2,H_2PtCl_6,$$

separates from hot alcohol and water in ill-defined crystals, and melts at 171°. The *methiodide*, $C_{12}H_{15}NO_2,MeI$, is formed by the direct combination of the base with methyl iodide in alcoholic solution; it crystallises from hot water in transparent, hexagonal prisms, melts at 216—217°, and is not decomposed by boiling concentrated alkalis. The *methochloride*, $C_{12}H_{15}NO_2,MeCl$, is obtained in the form of microscopic, hexagonal prisms when an aqueous solution of the methiodide is digested with silver chloride, and the filtrate evaporated; it crystallises from alcohol in lustrous plates melting at 211°. Its *platinochloride*, $(C_{13}H_{18}NO_2Cl)_2,PtCl_4$, is an indistinctly crystalline compound which melts at 221°, and is almost insoluble in water; the corresponding *aurochloride*, $C_{13}H_{18}NO_2Cl,AuCl_3$, is a yellow, crystalline, sparingly soluble substance melting at 153°. The *ammonium base*, $C_{12}H_{15}NO_2,MeOH$, is a strongly alkaline syrup, readily soluble in water.

Bromomethylhydrohydrastinine, $C_{12}H_{14}NO_2Br$, is obtained when methylhydrohydrastinine is treated with bromine in carbon bisulphide solution until a permanent coloration is produced, and the brown, semi-solid product agitated with dilute soda. It crystallises from hot water in octahedra, melts at 187°, and is soluble in alcohol.

Bromohydroxymethylhydrohydrastinine methiodide,



$$\mathrm{CH_2}<\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}>\mathrm{C_6H_2}<\begin{matrix}\mathrm{CH_2{\cdot}NMe_3I}\\\mathrm{C_2H_3Br{\cdot}OH}\end{matrix},$$

is formed when an aqueous solution of methylhydrohydrastinine methochloride is treated with bromine-water until a permanent coloration is produced, and the concentrated solution of the product mixed with potassium iodide; it crystallises from water in colourless prisms melting at 177°. F. S. K.

Pseudotropine. By C. Liebermann (*Ber.*, **24**, 2587).—The author has examined the products of oxidation of pseudotropine. The method employed is the same as that employed for the oxidation of ecgonine and tropine (Abstr., 1890, 1449; this vol., p. 749). The main product is tropic acid. It shows all the properties formerly assigned to this compound, has the same solubility in water and alcohol, has a strongly acid reaction, melts at 251°, and dissolves copper oxide and silver oxide. The silver solution deposits a metallic mirror on warming. The solution of the acid reduces potassium permanganate. The *copper* salt, dried at 125°, has the composition $C_8H_{12}NO_4{\cdot}CuOH$. Together with the above acid, ecgoninic acid is also obtained. E. C. R.

Alkaloïds of the Areca Nut. By E. Jahns (*Ber.*, **24**, 2615—2617; compare this vol., p. 94).—Further investigation has shown that both arecoline and arecaïdine exist ready formed in the areca nut, and that the latter is not derived from the former in the process of extraction. Arecaïdine and arecaïne are most easily separated by treatment with hydrochloric acid and methyl alcohol, since the former is thereby converted into its methyl derivative, arecoline, whilst the latter remains as hydrochloride.

The examination of larger quantities of material has led to the discovery of a fifth alkaloïd in areca nut. This has been termed guvacine, from guvaca, the Indian name for the areca palm. *Guvacine*, $C_6H_9NO_2$, forms small, lustrous, anhydrous crystals, melts at 271—272° with decomposition, and has a neutral reaction. It does not dissolve in ether, chloroform, benzene, or strong alcohol, but is tolerably soluble in water and dilute alcohol, although to a less degree than the other two crystalline alkaloïds. The salts crystallise well, have an acid reaction, and resemble the base in their behaviour with the ordinary solvents. The *hydrochloride*, $C_6H_9NO_2,HCl$, crystallises in broad, flat, anhydrous prisms, and is tolerably soluble in water, but only very sparingly in dilute hydrochloric acid; the *sulphate* forms silvery scales; the *nitrate* crystallises in lustrous prisms. The *platinochloride*, $(C_6H_9NO_2)_2,H_2PtCl_6 + 4H_2O$, crystallises from water in hexagonal prisms resembling those of the choline derivative, and melts at 211° with frothing and decomposition, whilst the *aurochloride*, $C_6H_9NO_2,HAuCl_4$, forms broad, flat prisms which melt at about 194—195°. Search is being made for other alkaloïds in the areca nut. W. P. W.

Lupinidine from White Lupines (Lupinus albus, Lin.). By G. Campani and S. Grimaldi (*L'Orosi*, **14**, 19—24, and *Gazzetta*, **21**, 432—437).—After an historical review of the subject, the authors describe their method of preparing considerable quantities of the extract of lupines, and of separating the alkaloïd as platinochloride. This salt has the composition $(C_8H_{15}N)_2,H_2PtCl_6 + 2H_2O$, as stated by Baumert (*Annalen*, **224**, 325). The free alkaloïd, *lupinidine*, $C_8H_{15}N$, when freshly prepared, is a pale-yellow, heavy, oily, alkaline liquid, with an extremely bitter and pungent taste; it is freely soluble in water and alcohol, but only sparingly in ether. It hardens on exposure to air, acquiring a yellowish-brown colour. If it is kept for a few days in a sealed tube, groups of white, acicular crystals separate, and gradually increase until the presence of liquid is almost concealed. This is probably due to the presence of a crystallisable hydrated lupinidine, $C_8H_{15}N,H_2O$, side by side with the anhydrous alkaloïd. According to Bufalini, 0·5 c.c. of the solution of the hydrochloride causes death in frogs in a couple of hours, symptoms of general paralysis being previously induced. S. B. A. A.

Formation of Carbamide by the Decomposition of Arginine. By E. Schulze and A. Likiernik (*Ber.*, **24**, 2701—2704).—When arginine (compare Schulze, this vol., p. 857) is boiled with a saturated solution of barium hydroxide, it is decomposed with formation of carbamide; it shows, therefore, a behaviour similar to that of lysatine (compare Drechsel, this vol., p. 95). F. S. K.

Heat-coagulation of Proteïds. By J. Corin and Q. Ausiaux (*Bullet. de l'Acad. roy. de Belgique*, **21**, 345—361).—In a number of experiments made with ox-serum, the statement made by Halliburton (*J. Physiol.*, **5**), that two serum-albumins, separable by fractional heat-coagulation, are present, is confirmed. The temperatures of coagulation found were 73—74° and 79—80° respectively. These temperatures are rather lower than those given by Halliburton, as the true temperature of coagulation is taken as the point when opalescence first occurs. In this last point they agree with Haycraft and Duggan, but differ from them in finding that the concentration of a solution of proteïd has very little influence on the temperature of coagulation; the acidity, however, must be kept constant.

W. D. H.

Toxalbumin Secreted by the Microbe of Blennorhagic Pus. By Hugounenq and Eraud (*Compt. rend.*, **113**, 145—147).—Peptonised beef tea that has served for the cultivation of the micrococcus of blennorhagic pus, when filtered through porcelain and mixed with excess of alcohol, yields a solid substance, which, when redissolved in water, again filtered through porcelain, and again precipitated by alcohol, yields an amorphous, yellowish-white solid, very soluble in water, and resembling the albuminoïds in its chemical and physical properties. It is not coagulated by heat, or by nitric acid, is slowly precipitated by potassium ferrocyanide and acetic acid, but not by magnesium sulphate. It has no diastatic action on starch, sugar, or fibrin, and, when exposed to air in a moist condition, it putrefies rapidly, with development of a very peculiar odour. It leaves no appreciable residue on incineration, contains phosphorus and 11·45 per cent. of nitrogen, but is free from sulphur. A solution of the toxalbumin sterilised by filtration has no injurious effect when injected under the skin of the dog, and placed on the eye, or in the urethra, but if injected into the testicle it causes suppuration and complete atrophy. No similar effects are produced by the sterilised beef tea or the peptone.

If a solution of asparagine containing meat ashes is used as the cultivation fluid, the microbe develops more slowly, and no toxalbumin is formed. It follows, therefore, that the latter is not simply a secretion of the microbe, but results from its action on the peptone.

C. H. B.

Conversion of Carboxy-hæmoglobin into Methæmoglobin, and Detection of Carbonic Oxide in Blood. By H. BERTIN-SANS and J. MOITESSIER (*Compt. rend.*, **113**, 210—211).—The authors find that, contrary to the statements of Weil and of von Anrep, when carboxy-hæmoglobin is mixed with potassium ferricyanide, no compound of carbonic oxide and methæmoglobin is formed, but the product is simply a solution of carbonic oxide in a solution of methæmoglobin, from which it is expelled by the passage of hydrogen or carbonic anhydride, or by being placed in a vacuum, as easily as it is from its solution in water.

In order to detect carbonic oxide in blood, the latter is diluted with twice its volume of water, and mixed with sufficient powdered potassium ferricyanide to ensure complete conversion into methæmoglobin. The flask is then made vacuous, and the gas pumped out is passed into a solution of oxyhæmoglobin contained in a suitable absorption tube. With 400 c.c. of blood, a quantity of carbonic oxide amounting to only one-fifteenth of its volume, can be recognised. C. H. B.

Physiological Chemistry.

Diastatic Action of Human Saliva. By A. SCHLESINGER (*Virchow's Archiv*, **125**, 146—181, and 340—363).—The diastatic activity of saliva was estimated in a number of cases of healthy and diseased persons. The smallest ferment activity was found in a case of diabetes mellitus (0·42 per cent.), and in a case of phthisis (0·45). The other cases of diabetes show a slight diminution, as do also the other cases of phthisis, typhoid, chronic nephritis, mercurial salivation, iodism, articular rheumatism, dyspepsia, cancer, and jaundice. In spinal paralysis, no difference was observed. The eight normal cases showed only slight differences; the greatest difference being 0·097 (0·878 and 0·781). In young children, the ferment activity is rather less than in adults.

The addition of an alcoholic solution of thymol for antiseptic purposes lessened the diastatic activity in one-half of the normal, and one-third of the pathological cases; in the remaining two-thirds, it did not; the hindering influence is believed to be due both to the thymol and the alcohol, chiefly on the bacteria in the saliva, which appear to be more abundant in pathological than in healthy saliva. A very complete history of the subject and bibliography are given.

W. D. H.

Gelatin as a Reagent for the Detection of Tryptic Enzymes. By C. Fermi (*Chem. Centr.*, 1891, ii, 87; from *Arch. Hygiene*, **12**, 240—260).—In place of fibrin, the author has successfully employed gelatin as a means of detecting the presence of proteolytic enzymes. The gelatin is prepared from 5—10 grams of pure gelatin, and 93 grams of aqueous thymol or phenol solution; 5—10 c.c. of this gelatin is run into a test-tube, allowed to solidify, and the solution under examination, to which a little thymol or phenol has been added, is run on to the surface. If at the end of five or six days the gelatin shows no signs of liquefying, the absence of enzymes is established. By means of this reagent placed in graduated cylinders, the author has been enabled to study the properties of the unorganised ferments, and their behaviour with animal and vegetable tissues.

J. W. L.

Neutral Sulphur and Metabolism. By Rudenko (*Virchow's Archiv*, **125**, 102—114).—In addition to the sulphur present in the urine as sulphates (preformed and ethereal), there is an organic substance or substances, which contain the so-called non-oxidised or neutral sulphur. The amount of this present varies considerably, and a quantity of it was prepared from dogs' urine. The following general conclusions from experiments and observations in cases of disease are given:—

(1.) Many processes which increase the decomposition of the body proteïds do not raise also the power of oxidation, but lessen it. This is indicated by the lactic acid which appears in the urine in phosphorus poisoning, the sugar in carbonic oxide poisoning, and the sarcolactic acid that occurs in the urine during artificial dyspnœa (Hoppe-Seyler) comes under the same category.

(2.) In certain circumstances, not well explicable, the neutral sulphur administered to dogs undergoes complete oxidation in the body; but the separation from the organism takes much longer than if the same element were given combined as sulphuric acid.

W. D. H

Influence of Sulphonal on Proteïd Metabolism. By M. Hahn (*Virchow's Archiv*, **125**, 182—188).—Several observers having shown that certain narcotics increase nitrogenous metabolism, it was considered advisable to investigate the question so far as it relates to sulphonal. A series of observations were made on a dog, for periods without, and for periods with, the administration of the drug, in addition to the food. The body weight, the nitrogen ingested and excreted, the sp. gr. and amount of the urine, and the sodium chloride in it, are given in tabular form. The periods during which sulphonal was given were two in number. The first produced an increased output of nitrogen, which lasted for a week or more after the drug was stopped. In the second experiment, the excretion of nitrogen was somewhat diminished, but there was a good deal of diarrhœa, which increased the difficulties of the experiment, which therefore demands repetition. In both cases the output of sodium chloride was increased. W. D. H.

Tissue Fibrinogens. By A. E. WRIGHT (*Brit. Med. Journ.*, ii, 1891, 641—644).—Wooldridge's "tissue fibrinogens" were prepared from testis and thymus by precipitating them from an aqueous extract of the organs by means of acetic acid. They were found to give the biuret reaction, and the nitric acid test for proteoses, but the opinion is expressed that they are not proteoses, but substances from which proteoses are readily formed. Further investigation showed that they were nucleo-albumins. The question whether injection of solutions of tissue fibrinogens acts protectively against the *Bacillus anthracis* was tested on rabbits. The results are inconstant, but tend to show that there is a certain amount of immunity produced.

W. D. H.

Decomposition of Albumin in Fasting. By I. MUNK (*Bied. Centr.*, **20**, 521—522; from *Cent. Med. Wiss.*, **27**, 833—836).—In opposition to Klemperer's view that the value for the loss of nitrogen (average 11·3 grams a day) obtained in the fasting experiment made on Cetti by Senator, Zuntz, and others was high owing to tuberculosis the author obtained exactly the same mean result in an experiment with a perfectly healthy man who fasted for six days. Voit obtained the same result in a series of experiments with young men. Finally Succi, during a fast of 10 days, lost an average daily amount of 10·7 grams of nitrogen. The chief factors which determine the loss of nitrogen are the small amount of fat in the body and the large amount of water consumed. It was observed that on the two days following the fast, when albumin (101 grams), fat (139 grams), and carbohydrates (309 grams) were given, only 54 grams of albumin was decomposed and quite 40 grams deposited; owing to the consumption of non-nitrogenous matter, the loss of nitrogen was reduced to 8·3 grams. N. H. M.

Influence of Increased Muscle Activity on the Decomposition of Albumin. By F. HIRSCHFELD (*Bied. Centr.*, **20**, 519—520; from *Centr. Med. Wiss.*, **29**, 66—67).—The author, in experiments made on himself, estimated the daily nitrogen secretions, first, with a mixed diet containing albumin (162 grams), fat (167 grams), and carbohydrates (327 grams); and then with a diet containing albumin (37—43) grams, fat (164—183 grams), and carbohydrates (379—408 grams). The increased muscle activity consisted in doing hard work for six hours daily, and in ascending 400—500 metres. With sufficient food, it was found that the decomposition of albumin was not increased, whether the food contained much or little albumin. If, however, the food is insufficient, a considerable loss of albumin takes place. During three days of rest the author lost 1·5, 2·1, and 4·6 grams of nitrogen, and during three days, on which he worked, 2·1, 5·1, and 6 grams of nitrogen. The results explain those of Argutinsky, who found the amount of albumin decomposed after muscular exertion to be increased when the feeding was insufficient. N. H. M.

Importance of Asparagine for Feeding. By J. König (*Bied. Centr.*, **20**, 515—516; from *Centr. Med. Wiss.*, **28**, 849—852).—After Pfeiffer and Schulze showed that in germinating plants, asparagine is formed from decomposing reserve albumin, that the asparagine remains as such in air free from carbonic anhydride, whilst in presence of carbonic anhydride it disappears, probably again yielding albumin, it seemed likely that asparagine might in the animal organism be regenerated into albumin when a food is used which is poor in nitrogen but rich in carbohydrates; or at least, that it might economise albumin. The experiments of Weiske, Kennepohl, Schulze, and others with rabbits, fowls, geese, sheep, and cows supported this view, showing that asparagine gives rise to deposition of albumin and to increased milk production. On the other hand, Munk found that in the case of a dog fed exclusively with meat, or with a mixture of meat and carbohydrates, there was no diminution, but rather a slight increase, in the amount of albumin lost. Knieriem, who also experimented with a dog, found no increase in the amount of urine when asparagine was given. v. Voit and Politis, in experiments with rats, found that asparagine did not give rise to any saving of albumin. The results of Zuntz and Hagemann pointed to the same conclusion. The author considers the question to be still an open one. N. H. M.

Influence of Acid Mineral Salts on the Composition of Bones. By H. Weiske (*Landw. Versuchs-Stat.*, **39**, 241—268; compare this vol., p. 848).—The experiments were again made with rabbits; they were all of the same litter, and were 107 days old. The object was to ascertain the effect of a food with an alkaline ash (hay) with or without oats, as compared with a food which gives an acid ash (oats), and partly with addition of dihydrogen sodium phosphate. The exclusive use of oats might have some action, and the addition of the acid salt would intensify the action. The urine of the rabbits fed with hay (0) and with hay and oats (1 and 2) was alkaline, but where oats was given alone (3 and 4) and with the salt (5 and 6), the urine was respectively distinctly and strongly acid. The following table shows the initial and final weights in grams of each rabbit (the experiment lasted three months), and the weight of the dry, fat free skeletons:—

No.	0.	1.	2.	3.	4.	5.	6.
Initial weight..	1750	2030	1830	1900	1915	2040	1925
Final weight ..	2430	3480	3360	2320	1740	2160	1460
Skeleton	87·66	115·92	115·59	74·13	64·44	67·15	60·37

There was thus a considerable difference in the weight of the bones with the different feeding, Nos. 1 and 2 (fed with hay and oats) being much the heaviest, and 3—6 the lightest. The latter in the fresh condition are, however, relatively the heavier. The bones of 0, 1, and 2 were thicker and harder than the others; those of No. 6 were very thin and breakable. The percentage of ash in the short bones (*a*), the long bones (*b*), and the teeth (*c*) was as follows:—

	0.	1.	2.	3.	4.	5.	6.
a	62·13	60·40	62·70	57·22	60·26	—	58·47
b	66·51	66·29	67·00	60·85	63·46	—	63·38
c	78·72	77·26	78·59	75·68	79·53	—	80·01

With regard to the ash constituents, the differences are not great; but the percentages of lime, phosphoric acid, and carbonic anhydride are generally lower in the ashes of 3 and 6 than of 0, 1, and 2. The magnesia is either the same or higher in 3 and 6 than in the others. But it is rather the amount of ash which varies than the composition. The extraction of mineral matter from the bones is caused by the acid nature of the food. Although of the three normally fed rabbits No. 0 had the lightest skeleton, the percentage amount of total ash and ash constituents was approximately equal in all three; whilst the bones of the other rabbits contained not only absolutely but relatively less ash, and were in part very thin-walled and little capaple of resistance. N. H. M.

Action of Sugars in the Body. By P. Albertoni (*Chem. Centr.*, 1891, ii, 44; from *Ann. Chim. Farm*, **13**, 145—159).—Sugar was administered to dogs, which had fasted for 24 hours, and at the end of a given time they were killed by admitting air into the veins. The contents of the stomach were then collected and examined. Experiments were made with maltose, cane sugar, and lactose. Maltose, and especially cane sugar, are absorbed more quickly than glucose. In an hour 70 to 80 per cent. was absorbed. Lactose, however, is different, the amount absorbed being only from 20 to 40 per cent. The absorption is especially small if the solutions are denser than the blood. There is always a certain quantity of sugar found in the tissues outside the stomach. Dilute solutions of lactose are more easily absorbed, the proportion in which it is contained in milk being the most advantageous. Lactose and levulose act on the circulatory system partly like, and partly unlike, glucose, maltose, and cane sugar. The former do not increase the blood pressure, but lessen the pulse frequency; the latter cause a rise of 10—20 mm. in pressure. This is due to their direct action on the blood. Sugar absorbed by the natural channels does not increase the body temperature. W. D. H.

Formation of Glycogen in the Liver. By E. Nebelthau (*Zeit. Biol.*, **28**, 138—176).—In the present research, hens and rabbits were the animals chiefly employed, and the principal investigations relate to the influence of certain drugs on the liver glycogen; the animals used had been deprived of food for some days previous to the experiments, and were killed as nearly as possible the same length of time after the administration of the drug. The work of Röhmann is criticised, as he did not pay attention to this latter point; from 20—24 hours after the administration of food or drug being the time when the maximum of glycogen is found. In some cases, the glycogen in the muscles was estimated also, in all cases by Külz's method. The danger of trusting implicitly to single control animals is pointed out, as the glycogen varies greatly in animals treated in precisely the same way. Full tables of analyses are given throughout.

Chloral hydrate was found to increase the hepatic glycogen, the lethargic condition induced by this drug, and the consequent comparative immobility of the animals, tending to its accumulation; this suggested similar investigations regarding other narcotics; the increase was always found after the administration of chloralamide, paraldehyde, and sulphonal; occasionally the same was observed after the injection of ether, chloroform, and alcohol. Urethane did not produce a marked effect; in only two out of seven experiments was there a slight increase of glycogen in the liver.

Ammoniacal compounds are stated by Röhmann (*Pflüger's Archiv*, **39**, 21) to cause increase of the glycogen in the liver; this led him to certain general conclusions regarding the part played by nitrogenous compounds in the formation of carbohydrate material in the body; in the present research, ammonium citrate, ammonium formate, benzamide, formamide, ammonium lactate, and asparagine were used. On the whole, the results obtained confirm those of Röhmann; all increase the liver glycogen; this is true also for lactic acid compounds, which, according to Röhmann, have not this effect.

The febrifuges, antipyrin, kairin, and quinine, all increase the hepatic glycogen. So does section of the cervical spinal cord; this is a confirmation of an old observation of Claude Bernard's.

W. D. H.

Specific Gravity of Blood. By E. L. Jones (*J. Physiol.*, **12**, 299—346).—Further observations on the sp. gr. of the blood under various conditions (compare Abstr., 1887, 608) led to the following results.

1. The sp. gr. of the blood varies in different parts of the body, but that from any part bears, *cœt. par.*, a definite relation to that taken from any other part. It is usually the same in corresponding parts of the symmetrical halves of the body. Variations in blood supply to any part are the most frequent causes of alteration of the sp. gr. there, while it remains unchanged elsewhere.

2. The sp. gr. is very high in birds, and low in such animals as frogs.

3. The sp. gr. varies considerably in different persons; it is generally lower in women than in men; before the fifteenth year it is about the same in both sexes; it is higher in old women than old men. In males, the sp. gr. is about 1·066 at birth, and falls gradually for three years to 1·050; then it rises till about the seventeenth year, when it is about 1·058; it remains at about this height till old age comes on, when it falls slightly. In females the chief difference from the foregoing is that during the greater part of life it is 1·0555 instead of 1·058. In girls from 15 to 22 the limit consistent with health is very low, and chlorosis appears to be an exaggeration of this physiological condition.

Further extensive data are given respecting the variations in sp. gr. with complexion, race, physique, food, exercise, sleep, menstruation, anæmia of various kinds, heart diseases, kidney diseases, various fevers, phthisis, syphilis, and many other diseases. W. D. H.

Glycolysis in the Blood. By M. ARTHUS (*Arch. de Physiol.*, 1891, 425—439).—Lépine and Barral have described in the blood, probably derived from the white corpuscles, a ferment which has the power of destroying sugar, and the absence of which they consider to be a cause of diabetes. In the present experiments, it was found that glycolysis in the blood is a phenomenon of fermentation, but the ferment is absent in the circulating blood. It is formed when the blood is shed, as a result of the disintegration of formed elements other than the red corpuscles. Glycolysis in the blood is thus a cadaveric phenomenon like coagulation. W. D. H.

Influence of Acids and Alkalis on the Alkalinity of Human Blood, and on the Reaction of the Urine. By A. FREUDBERG (*Virchow's Archiv*, **125**, 566—600).—The alkalinity of the blood was estimated by a slight modification of v. Jaksch's method of titrating small quantities with very dilute tartaric acid. Recent researches by Bohr have shown that estimation of the carbonic anhydride leads to an incorrect estimate of the alkalinity. The reaction of the urine was estimated by titration with normal soda solution or normal oxalic acid according as the original urine was acid or alkaline respectively. The result of a great number of observations on the blood and urine of patients suffering from a variety of diseases, and also after the administration internally of various acids and alkalis, are given in tabular form, from which the following general conclusions are drawn:—

Hydrochloric acid (4—8 grs. of the officinal acid per diem) does not alter the alkalinity of the blood. Only one exception was noted. The acidity of the urine is, however, always increased.

Lactic acid (10—30 grs.) lessens the alkalinity of the blood by one-fifth to one-fourth. The acidity of the urine is increased, but not markedly so, and not in a degree corresponding with the amount of acid given. It is no doubt to a large extent oxidised in the body.

Tartaric acid (5—10 grs.) lessens the alkalinity of the blood by one-sixth; it also increases the acidity of the urine, but not markedly. It also is burnt to a great extent in the body.

Sodium hydrogen carbonate (5—15 grs.) in three cases increased the alkalinity of the blood by one-fourth; in two other cases there was no change. In all cases the urine was strongly alkaline.

W. D. H.

Xanthine Substances in Urine. By G. SALOMON (*Virchow's Archiv*, **125**, 554—556).—Previous investigations having shown that xanthine, paraxanthine, and heteroxanthine are constituents of normal urine, and can be obtained in small quantities from large volumes of urine, the present research is directed to ascertaining whether they can be demonstrated to exist in smaller quantities of urine. The property of the para- and hetero-compounds to form sparingly soluble crystalline compounds with sodium or potassium hydroxide is the most important reaction for separating the members of the group; after the precipitation of these compounds, xanthine remains in solution. The distinction between paraxanthine and heteroxanthine requires the use of more material, and can be accomplished by the corrosive sublimate and picric acid reactions.

The crystalline compounds of paraxanthine and heteroxanthine with sodium hydroxide are figured, and there is a description of their crystallography. They melt about 300°. The compounds with potassium hydroxide have similar reactions, and a higher melting point.

The paper concludes with a brief account of 21 observations of human urine. In normal urine, paraxanthine appears to be the member of the group most frequently present; in seven cases of various diseases, although the soda reaction was always successful, paraxanthine was sometimes absent. W. D. H.

Oxidation of Aromatic Substances in the Animal Organism. By K. Klingenberg (*Chem. Centr.*, 1891, ii, 39—40; from *Diss. Rostock Inst. Pharm. physiol. Chem.*).—Aromatic substances belonging to various groups were given to dogs, and their urine for the 24 hours following was examined, with the following results:—

1. Diphenyl is changed in the organism to, and excreted as, parahydroxydiphenyl.

2. Benzidine behaves similarly to quinone, is non-toxic, and is excreted unchanged.

3. Paradibromodiphenyl is also not poisonous, and undergoes no oxidation in the body.

4. Paramidodiphenyl kills in two hours, changing the pigment of the blood corpuscles to methæmoglobin.

5. Carbazole is not poisonous, and is oxidised in the body to hydroxycarbazole, leaving it by the urine as an ethereal hydrogen sulphate.

6. Fluorene is not poisonous. No increase in the ethereal hydrogen sulphates is found after its administration.

7. Phenanthrene and phenanthraquinone are both very well borne. They probably act as antiseptics, and diminish the output of combined sulphuric acid. Glycuronic acid compounds were not found in the urine.

8. Diphenylamine is oxidised in the body to parahydroxydiphenylamine.

9. Diphenylmethane is changed in the body to parahydroxydiphenylmethane.

It thus appears to be the rule that the hydroxylation of aromatic substances within the body, as well as outside of it, consists in the formation of substitution products in which hydroxyl occupies the para-position. If the para-position is already occupied, no hydroxylising action follows. W. D. H.

Formation of Glycuronic Acid during Inanition. By E. Nebelthau (*Zeit. Biol.*, **28**, 130—137).—Thierfelder (Abstr., 1886, 572) states that during inanition, and after the administration of chloral hydrate, glycuronic acid in combination as urochloralic acid is found in the urine. The animals with which he experimented had received no food for six days previous to the experiments. Considering that this length of time is sufficient for the complete disappearance of all the glycogen of the body, he concludes that in the appearance of glycuronic acid in the urine he has proof of the formation of carbohydrate from proteïd. Without at all denying this possibility, the present paper points out that Thierfelder's experiments do not prove it, as, after six days' hunger, there is always a considerable amount of glycogen left, both in the liver and in the muscles. The glycogen was estimated by Külz's method. W. D. H.

Elimination of Urea in Fever. By H. C. Wood and J. Marshall (*Journ. of Nervous and Mental Disease*, 1891, 1—9).—It is well known that the amount of urea eliminated during fever is greater than the normal. It seems, however, not to be settled whether this is an integrant part of the febrile process, or caused by the action of the excessive heat on certain organs, or by some of the derangements of the bodily functions produced by fever. The latter theory seems probable, as Schleich (*Arch. Exper. Path. u. Pharm.*, **4**) and Naunyn (*Berlin klin. Woch.*, 1869), in dogs, and Bartels (*Greifswalder med. Beit.*, **3**, 1864), in man, found that artificial elevation of the body temperature produced an increased output of urea.

Many clinical observers have noted that the increased elimination of urea is not necessarily proportionate to the body temperature, and that in the crisis of the fever there is apt to be an extraordinary amount excreted, although the body temperature may be normal or even subnormal; and that in many diseases with low temperature, like cancer, scurvy, diabetes, gout, and especially various affections of the liver, there is again a great increase in urea elimination. In this relation, cases of hepatic fever (that is, the fever produced by stones in the gall-bladder or ducts) become important. The general results of previous and the present experiments show that, even in hepatic fever, a distinct rise of temperature is usually accompanied with an increase in the elimination of urea.

It is, however, most important to remember that temperature is not necessarily a measure of fever; there may be increased heat production, even when the body temperature is below the normal. It is evident that careful calorimetrical studies are urgently needed, by which a comparison may be made between heat production (instead of body temperature) and urea elimination. It may be, for instance, that heat production is much increased during the crisis of a fever. This would explain the critical increase of urea.

The opposite question then arises, whether intense fever with great increase of heat production can exist without corresponding increase in the excretion of urea. Two experiments were made on dogs, which answer this question in the affirmative; after fasting for 24 hours, the urea eliminated was measured for 12 hours, and then the medulla divided at its junction with the pons. This leads to an excessive production of animal heat. The animals lived a few hours after the operation, and the urea excreted during that time was estimated; the results were as follows:—

	Before operation.		After operation.	
	Time.	Urea.	Time.	Urea.
Dog 1	12 hours	10·5 gr.	9 hours	0·9 gr.
Dog 2	12 ,,	8·3 ,,	6 ,,	2·1 ,,

No urea was found in the blood of either animal. Division of the spinal cord produces no constant result. W. D. H.

Therapeutic and Physiological Effects of Ozone. By D. LABBÉ and OUDIN (*Compt. rend.*, **113**, 141—144).—Ozone, prepared by the chemical method, is always impure and poisonous, owing to the presence of phosphorous acid. The authors employ an ozone generator, consisting of a closed glass tube containing rarefied air (which acts as one of the poles), surrounded by a tube on the inner surface of which is a metallic thread. The space between the tubes is 3—4 mm., and across this space pass the sparks that produce the ozone. The tubes being fixed vertically, the slight rise of temperature resulting from the discharge causes a continuous upward current of ozonised air, which mixes with the unaltered air in the apartment. Under these conditions, if care be taken that the quantity of ozone does not exceed 0·011—0·012 milligram per litre, the ozonised air can be breathed even by young children without injurious effect. When the atmosphere is breathed by anæmic subjects, there is a rapid increase in the quantity of hæmoglobin in the blood. Cultivations of the bacillus of tubercle on peptonised gelatin seem to be completely sterilised by the action of the ozonised air.

Ten tubes of the kind described, each being about 800 mm. long, were placed in a laboratory of 300 cubic metres air space, and were actuated by an alternating current from a Gramme machine with a potential of 7000 volts. After about a quarter of an hour, the laboratory was filled with a bluish cloud of aluminium or aluminium oxide, and direct experiment showed that the electric discharge caused the volatilisation of weighable quantities of aluminium from the electrodes. C. H. B.

Quinine as a Protoplasmic Poison. By C. BINZ (*Virchow's Archiv*, **125**, 196—197).—In Hermann's *Handbuch*, Engelmann speaks sceptically concerning Binz's observation on the deadly influence of quinine on amœboid movement. The latter observer now publishes a letter from Engelmann, with an enclosure of a dissertation by ten Bosch, one of his pupils, in which it is shown that Binz is correct, and, moreover, that quinamine has only one-sixth of the toxic power of quinine on protoplasm. W. D. H.

Saponins. By R. KOBERT (*Chem. Centr.*, 1891, ii, 176; from *Pharm. Centralhalle*, **30**, 335).—The author considers that there are a series of saponins of the general formula $C_nH_{2n-8}O_{10}$, several of which are known. Saponins of the same formula and of the same chemical properties appear to have different physiological characteristics, and show great differences in their poisonous action. The sapotoxin of *Agrostemma githago* (corn cockle), one of these substances, is absorbed both by the subcutaneous tissues and by the intestinal canal, and thus acts as a dangerous poison. It is recommended that, before using this seed as a food, the shell and embryo shall be separated.

J. W. L.

Chemistry of Vegetable Physiology and Agriculture.

Manufacture of Pure Yeast. By H. ÉLION (*Bull. Soc. Chim.* [3], **5**, 451).—The author describes and figures a steriliser and a fermenting apparatus which is capable of yielding 10 kilos. of absolutely pure yeast at each charge. (Compare Fernbach, this vol., p. 352.)

T. G. N.

Action of Hydrogen Fluoride and of Fluorides on Yeast. By J. EFFRONT (*Bull. Soc. Chim.* [3], **5**, 476—480; compare this vol., pp. 477 and 488). Hydrogen fluoride, when present in fermenting saccharine solutions, retards the activity of yeast, and 5·5 milligrams of hydrogen fluoride per 100 c.c. will arrest the fermentation. Small amounts of potassium fluoride (up to 5·5 milligrams per 100 c.c. of solution) augment the activity of the yeast, and although an excess of this salt has a deterrent effect on the fermentation of cane sugar dissolved in distilled water, the quantity may be increased, with beneficial results, to 50 milligrams per 100 c.c. of a wort containing nutrient materials.

T. G. N.

Bread Fermentation. By L. BOUTROUX (*Compt. rend.*, **113**, 203—206).—In leavens to which no yeast had ever been added since time immemorial, the author always found yeasts, and he isolated five distinct species, two of which are very active in producing alcoholic fermentation. From the flour, he isolated three distinct species of bacteria: α, which secretes a diastase that dissolves cooked gluten and saccharifies starch paste, but does not attack sugar; β, which produces fermentation, with evolution of gas, in a mixture of flour and water sterilised by heat; and γ, obtained from the bran, which produces a fermentation, with evolution of gas, in a mixture of bran and water. Bacillus α followed by yeast produces alcoholic fermentation.

Direct experiment showed that the yeasts active in producing alcoholic fermentation can readily be cultivated in paste, but this is not the case with the yeasts little active in alcoholic fermentation, nor with the bacteria α, β, γ. The yeasts can be cultivated in paste containing 0·3 per cent. of tartaric acid, but this quantity of acid completely prevents the "rising" of paste to which no leaven has been added, a result which shows that the yeast is the essential agent in bread fermentation, and if the bacteria play any useful part, it is only in the production of the sugar.

Flour charged with its natural microbes, mixed with salt water and pure yeast, and allowed to "rise," contains practically the same proportion of gluten as the original flour, and hence the fermentation of the glucose is not essential, but is a perturbation. Starch also is not affected to any great extent during the process. An aqueous extract of bran, freed from bacteria, saccharifies starch paste, but not crude starch, and this is true also of the amylose secreted by bacillus α. The only fermentable material that remains is the soluble part of the flour containing the preformed sugar, dextrin, and salts. The author concludes that bread fermentation consists essentially of the alcoholic fermentation of the sugar pre-existing in the flour. The yeast not only produces the gas that aërates the bread, but it also prevents the development of the bacteria. The difficulty of detecting the yeast in the paste arises from the intimate manner in which it is mixed up with the dough, but the presence of the yeast cells is more readily recognised than the presence of bacteria. C. H. B.

Nitrogen Assimilation of the Leguminosæ. By F. NOBBE, E. SCHMID, L. HILTNER, and E. HOTTER (*Landw. Versuchs-Stat.*, **39**, 327—359).—The objects of the experiments were (1) to include some kinds of papilionaceous woody plants, (2) to infect with pure cultivations of bacteria from (*a*) soil and (*b*) root nodules, as well as with soil extracts, (3) to ascertain whether one and the same bacterium produces nodules in all leguminous plants, or whether the various orders have their special organisms. The first series of experiments included *Pisum sativum*, *Robinia pseudacacia*, *Cytisus laburnum*, and *Gleditschia triakanthos*. The plants were grown in pure, sterilised sand containing 5 per cent. of powdered peat and 0·5 per cent. of pure chalk, and watered with a nutritive solution containing potassium chloride (0·0161), magnesium sulphate (0·0121), dihydrogen potassium phosphate (0·0133), and ferric phosphate (0·0033 per cent.). The peat was found to be injurious, owing to the formation of acids, and especially so in the first pot of each set, in which no chalk was used. The vessels were of glass and held 6·5 litres. The seeds were sterilised, and were allowed to germinate in sterilised water. The sand in the pots was covered with cotton wool, and the whole heated at 95°. There were 12 pots (5 plants in each pot) which were seeded as follows:—(2) Lupin soil extract, (3) pea soil extract, (4) *Gleditschia* soil extract, (5) *Robinia* soil extract, (6) *Cytisus* soil extract; all these were seeded 7th June; (7) pure cultivation of pea nodule bacteria, (8) pure cultivation of *Robinia* nodule bacteria (both seeded 27th June). Nos. 9—12 were not seeded, but (10) had calcium nitrate (0·973 gram on 8th July), and (12) had ammonium sulphate (0·803 gram on 30th June).

Pisum sativum.—The plants were set on the 21st May, and by the middle of June began to show nitrogen hunger. On the 27th of June, the pea soil extract (3) began to have an effect; and on the 30th, the plants seeded with *Gleditschia* (4) and *Cytisus* (6) soil extracts began to improve, whilst the *Robinia* soil extract (5) did not show effect until the 10th of July. The lupin soil extract had no effect at all (owing, perhaps, to its not being fresh enough), and the subsequent application of fresh soil extract also had no effect, being probably too late; the negative results obtained with Nos. 7 and 8 are also supposed to be due to the lateness of the application. Calcium nitrate, and ammonium sulphate, produced a beneficial effect two and three days after their application. The plants of both these pots produced flowers, whilst not one of the successfully infected plants did. On the other hand, almost all of the plants which did not recover from their state of nitrogen hunger (Nos. 2, 7, 8, 9, and 11), in spite of their scanty growth, produced flowers, and some even small fruit. The results confirm those obtained by Hellriegel, that the nodule bacteria give an impetus to vegetation, and hinder flower and fruit formation. All the successfully infected plants had nodules; one plant (in pot 4) had 4572 normal nodules. The nodules were almost all in the upper parts of the roots; this was also found to be the case in the experiments with other plants. The quantitative results as regards total produce and nitrogen are given in the table on next page.

Robinia pseudacacia.—The period of hunger began at the end of June and ceased first in the case of the plants seeded with the *Robinia* nodule bacteria (No. 8), and next where *Robinia* soil extract was given (5). The extracts of *Cytisus* and *Gleditschia* soil were slower in producing an effect; whilst the lupin and pea soil extracts, and the pea nodule bacteria, had no effect at all. Calcium nitrate, and ammonium sulphate, caused a distinct improvement two days after their application, and the plants so treated ripened soonest, and began to lose leaves when the infected plants were still quite fresh. The roots of the plants supplied with ammonia had no nodules, but those which had nitrate, and some of the unsuccessfully seeded pots had. It is at least possible for *Robinia* to exist without nodules (compare Frank, *Ber. deut. bot. Ges.*, 1890, 292). The nodules are generally larger, but less numerous, than on pea roots. All the successfully seeded plants had nodules. In the case of the plants infected with pea nodule bacteria, and of the other plants which were not intentionally infected, but which produced nodules, there was no increased growth. Frank's view that the bacteria have no object when the soil contains nitrogen seems to be correct. If it is assumed that the nitrogen assimilation takes place through the leaves, it is probable that the nodules in pots 2, 3, 7, and 9 were formed at a time when the roots still contained enough nourishment for them, but that the leaves were too much exhausted for the bacteria to enable them to recover. The results of the experiments indicate an essential difference in the behaviour of various soil extracts; *Robinia* soil extracts acted (with *Robinia*) the most quickly, and pea soil not at all, whilst other extracts were intermediate in their action. This point is further illustrated by special experiments described further on. Suitable infection had a greater vegetative action than an excess of ammonia or nitrate. The quantitative results—amount of dry produce, and the amount of nitrogen in produce, and in seed sown—are given, together with those obtained with peas, in the following table:—

	Seeding.	Dry produce (1 plant).			Nitrogen.		
		Stems and leaves.	Roots.	Whole plant.	In seed sown (1 seed).	In produce (1 plant).	Gain or loss.
	Pisum sativum.						
		grams.	grams.	grams.	gram.	gram.	gram.
2	Lupin soil extract	—	—	0·237	0·0057	0·0031	0·0026
3	Pea soil extract	—	—	1·806	0·0057	0·0364	0·0307
4	*Gleditschia* soil extract	2·888	0·430	3·318	0·0057	0·0687	0·0630
5	*Robinia* soil extract	1·696	0·662	2·358	0·0057	0·0477	0·0420
6	*Cytisus* soil extract	2·739	0·597	3·336	0·0057	0·0634	0·0577
7	Pea nodule bacteria (pure cultivations)	0·664	0·149	0·813	0·0057	0·0112	0·0055
8	*Robinia* nodule bacteria (pure cultivations)	0·783	0·182	0·965	0·0057	lost	—
9	not seeded 0·973 gram of calcium nitrate	0·311	0·132	0·433	0·0057	0·0054	0·0003
10		1·682	0·476	2·158	0·0057	0·0310	0·0255
11	0·803 gram of ammonium sulphate	0·264	0·100	0·364	0·0057	0·0052	0·0005
12		2·371	0·272	2·643	0·0057	0·0373	0·0316
	Robinia pseudacacia.						
2	Lupin soil extract	—	—	0·182	0·0011	0·0020	0·0009
3	Pea soil extract	—	—	0·175	0·0011	0·0020	0·0009
4	*Gleditschia* soil extract	1·826	1·643	3·469	0·0011	0·1096	0·1085
5	*Robinia* soil extract	2·248	1·471	3·719	0·0011	0·1098	0·1087
6	*Cytisus*	1·632	1·145	2·777	0·0011	0·0832	0·0821
7	Pea nodule bacteria (pure cultivations)	0·067	0·084	0·151	0·0011	0·0022	0·0011
8	*Robinia* nodule bacteria (pure cultivations)	2·040	1·468	3·508	0·0011	0·1136	0·1125
9	not seeded 0·973 gram of calcium nitrate	—	—	0·079	0·0011	0·0013	?
10		1·312	0·736	2·048	0·0011	0·0293	?
11	0·803 gram of ammonium sulphate	—	—	0·218	0·0011	0·0028	?
12		1·672	1·280	2·952	0·0011	0·0363	?

Cystisus laburnum.—There was no marked difference in the plants of the different pots by the 12th August, when the plants were taken up. On examining the roots, however, it was found that many of them had nodules, and it was noticed that the corresponding plants had new leaves still quite fresh. It seems probable that if the plants had been left longer, these plants would have continued to grow. No analytical results are given.

Gleditschia triakanthos.—No difference in the various plants was to be seen by the middle of July, and there were no symptoms of nitrogen hunger, but the plants grew very slowly. The plants supplied with nitrogen began to darken about eight days after the application. At the time of taking up (6th October), five plants in pot 10 and two in pot 12 were still healthy; all the others had lost all their leaves. The roots of all the plants were free from nodules. The dry matter of the produce (one plant) varied from 0·603 to 1·036 gram, and the nitrogen from 0·0085 to 0·0111 gram (one seed sown contained 0·0107 gram) in the pots where no nitrogen was given, so that there was, practically, no gain in any case. The ammonia and nitrate pots gave respectively (in one plant) 1·016 and 1·145 grams of dry matter and 0·0314 and 0·0306 gram of nitrogen.

As already shown by Hellriegel, extracts of various soils have quite different action on various plants; this depends not on the number (as Frank assumes), but on the kind, of organisms present.

The second series of experiments was similar to the first, except that only half the amount of peat was mixed with the sand. The plants were *Pisum sativum*, *Lupinus luteus*, and *Phaseolus vulgaris*, but the lupins did not grow well, owing, it is supposed, to unfavourable conditions of the sand.

Pisum sativum.—The plants were set on the 7th August, and were infected on the 14th with pure cultivations of bacteria from various sources as follows:—(1) Pea nodules, (2) pea soil, (3) lupin nodules, (4) lupin soil, (5) *Robinia* nodules, (6) *Robinia* soil. All the plants reached the period of hunger 14 days after the infection. Seven days later the plants of pots 1 and 2 began to acquire a darker colour, and five days later still the plants of pot 3 showed an increase of chlorophyll. The *Robinia* bacteria remained without action. When taken up (21st October), most of the plants had flowered; in the case of pots 1—3, the flowers fell off without forming fruit; whilst the small plants of pots 4—6 formed each one fruit with one seed. This result corresponds with that obtained in the first series with peas. The roots of the plants of pots 1—3 had all nodules; those of pots 4—6 had none. The nodules of pots 1 and 2 were very numerous, sometimes small and round, sometimes 2 mm. long and 0·8 mm. wide, and the bacteroïd tissues rose-coloured; the nodules of pot 3 grew into each other, sometimes extending 0·5 to 1 cm., and giving the root the appearance of being thickened. The nodules produced by pea nodule bacteria were formed on roots of the 2nd order; those produced by lupin nodule bacteria on roots of the 3rd order. The result of greatest interest is that the same (pea nodule) bacteria which, in another experiment, had no effect on *Robinia* produced nodules

2nd Series.

	Sources of bacteria used for seeding (pure cultivations).	Dry produce (1 plant).			Nitrogen.		
		Stems and leaves.	Roots.	Whole plant.	In seed sown (1 seed).	In produce (1 plant).	Gain or loss.
	Pisum sativum.						
		grams.	gram.	grams.	gram.	gram.	gram.
1	Pea nodules	1·441	0·245	1·686	0·0107	0·0573	0·0466
2	Pea soil	1·551	0·256	1·807	0·0107	0·0653	0·0546
3	Lupin nodules	0·878	0·184	1·062	0·0107	0·0350	0·0243
4	Lupin soil	0·314	0·158	0·472	0·0107	0·0083	−0·0024
5	*Robinia* nodules	0·311	0·135	0·446	0·0107	0·0072	−0·0035
6	*Robinia* soil	0·293	0·094	0·387	0·0107	0·0073	−0·0034
	Phaseolus vulgaris.						
1	Not seeded; calcium nitrate	0·746	0·327	1·073	0·0122	0·0177	?
2	Bean-soil extract itself	0·568	0·320	0·888	0·0122	0·0161	0·0039
3	Pea soil bacteria	0·818	0·401	1·219	0·0122	0·0231	0·0109
4	Lupin soil bacteria	0·605	0·361	0·966	0·0122	0·0140	0·0018
5	*Robinia* soil bacteria	0·716	0·327	1·043	0·0122	0·0176	0·0054
6	Pea nodule bacteria	0·797	0·308	1·105	0·0122	0·0184	0·0062
7	Lupin nodule bacteria	0·602	0·357	0·959	0·0122	0·0141	0·0019
8	*Robinia* nodule bacteria	0·578	0·308	0·886	0·0122	—	—
9	Not seeded	0·593	0·309	0·902	0·0122	0·0137	0·0015
10		0·661	0·382	1·043	0·0122	0·0152	0·0030

on the pea roots (the nodule formation being accompanied by much increased growth and nitrogen assimilation), whilst bacteria (from *Robinia* nodules), which had produced nodules on *Robinia* roots, had no effect on the peas. The numerical results are given with those obtained with beans in the table on the preceding page.

Phaseolus vulgaris.—The plants were set the 21st August, and infected on the 26th and 27th August, as follows:—No. 1, not infected, calcium nitrate, (2) bean soil extract, (3) pea soil bacteria, (4) lupin soil bacteria, (5) *Robinia* soil bacteria, (6) pea nodule bacteria, (7) lupin nodule bacteria, (8) *Robinia* nodule bacteria, (9 and 10) nothing. When taken up (27th November), the plants of pots 1, 4, 5, 7—10 were free from nodules; those infected with bean soil extract (2) and with pea soil and pea nodule bacteria (3 and 6) had numerous nodules; those of pot 3 being the largest. The view that beans produce nodules, even under sterilised conditions, is therefore erroneous. The nodules of the plants in pots 2 and 4 were in roots of the 3rd order, and from most of them there proceeds a root of the 4th order which often bears nodules, and is thicker than the root on which the nodule is situated. The roots have grown out of the nodule, and are remarkable on account of the large amount of crystals of calcium oxalate they contain at the point where they arise, proving that, in the roots as well as in the nodules, lively chemical changes take place, the products of which are not carried up into the above-ground portions, but to the roots. Moreover, these observations indicate that the changes connected with the enriching of the plant with nitrogen take place in the nodules. This does not touch the question whether the bacteria assimilate directly the free nitrogen of the air or water, or whether, as seems more probable, the crude nitrogenous material is brought to them from the leaves. The table on the preceding page shows the results of the second series of experiments with peas and beans.

Photographs are given of some of the plants at different periods of growth, and, also, of some of the roots.

In order to show the effect of various nodule organisms in different plants under absolutely identical conditions, five pots were prepared, into each of which 1 lupin, 1 pea, 1 *Robinia*, 1 *Cytisus*, and 1 *Gleditschia* were planted. The pots were seeded with bacteria from (1) *Gleditschia* soil, (2) pea nodules, (3) *Robinia* nodules, (4) lupin nodules. No. 5 was not seeded. All the plants showed nitrogen hunger about a month after they were planted; afterwards each plant which had been infected with its own organism (except the *Cytisus* and *Gleditschia*) began to grow better than the others. Only the *Robinia* of series 1, the pea of series 2, the *Robinia* of series 3, and the lupins and *Robinia* of series 4 had nodules. The *Robinia* nodules of series 1 and 4 were small and few.

In the two series of experiments, the evaporation from the plants was ascertained by weighing every day, and so much water given as was necessary to keep the weight at 60 per cent. of the weight of saturation. The results obtained with peas and *Robinia* are shown in curves, and are of great interest, inasmuch as the evaporation is an approximate measure of assimilation and growth. N. H. M.

Artificial Infection of Vicia faba with Bacillus radicicola. By M. W. Beyerinck (*Forsch. a. d. Gebiete d. Agr. phys.*, **14**, 57—58; from *Bot. Zeit.*, 1890, 837).—Beans were grown in specially constructed pots, and the same precautions taken for keeping out air organisms as Prazmowski used in his experiments. Some of the plants were infected with *Bacillus radicicola* (from bean nodules), and others left unseeded. All the infected plants had nodules, whilst none of the uninfected plants had any: the presence or absence of potassium nitrate or ammonium sulphate had no influence on the infection.

When the bacteria are grown in agar-agar containing only salts and cane-sugar, the growth ceases as soon as the small amount of assimilable nitrogen present is used up. The assimilation of free nitrogen does not, therefore, take place under these conditions, and at a temperature between 10° and 20°. But the bacillus has the power of utilising the smallest traces of combined nitrogen (nitrate, ammonia, peptone, or amide) in presence of a carbohydrate, especially cane sugar. This power of taking up the minutest traces of nitrogen compounds throws a new light on the symbiosis. In the nodules, the last traces of combined nitrogen are accumulated as reserve albumin in presence of the carbohydrates of the plant, giving rise to a complete nitrogen exhaustion of the soil round them. The author is acquainted with another organism (*Streptotrix humifica*), which also, in presence of carbohydrates, causes a complete nitrogen exhaustion of the soil, but does not live in symbiosis with Papilionaceæ.

The various papilionaceous bacteria differ more than the author formerly assumed. *Vicia faba* infected with *Bacillus ornithopi* produced no nodules. The difference in the bacteria of beans and serradella (*Ornithopus sativus*) accounts for the fact that serradella was found free from nodules growing in a garden between beans which had numerous nodules. N. H. M.

Formation of Starch from Formaldehyde. By T. Bokorny (*Chem. Centr.*, 1891, ii, 120—121; from *Ber. deut. bot. Ges.*, **9**, 103—106).—In continuation of previous researches on the formation of starch from methylene dimethyl ether by algæ (*Landw. Versuchs-Stat.*, **36**, 229—242), the author has grown algæ (*Spirogyra majuscula*) in solutions containing sodium hydroxymethylsulphonate, and has observed the formation of very considerable quantities of starch. The experiments lasted five days, the vessels being kept in an atmosphere free from carbonic anhydride, and exposed to the light during the daytime. Blank experiments were carried out at the same time, with the result that, in these cases, no formation of starch occurred. In order to neutralise the sodium hydrogen sulphite which is formed from the sulphonate, a little dipotassium or disodium phosphate was added to the solutions.

The solutions contained 1 part of the sulphonate in 1000.

J. W. L.

Ripening of Cherries: Fermentation of Cherry and Currant Juice, and Colouring Matters of Red and Black Currants. By W. Keim (*Zeit. anal. Chem.*, **30**, 401—407).—The first part of the following research deals with the changes in chemical composition which take place during the growth and ripening of the fruit of *Prunus cerasus.* The variety experimented with was the early egriot, specimens of which were gathered from a single tree at intervals of 7—10 days. Table I gives the results of the analyses in percentages.

TABLE I.

Date of gathering.	Average weight in grams.	Water per cent.	Dry substance per cent.	Total acid calculated as malic acid per cent.	Invert sugar. per cent.
15th May, 1890 ..	0·6375	88·88	11·12	0·213	2·74
21st May, 1890 ..	0·8259	83·73	16·27	0·310	3·13
28th May, 1890 ..	1·321	82·13	17·87	0·412	4·14
10th June, 1890..	3·08	83·63	16·35	0·421	9·12
19th June, 1890 .	3·719	81·223	18·777	0·462	10·26

Date of gathering.	Saccharose per cent.	Ash. per cent.	Acids present.	Glucoses present.
15th May, 1890....	0·187	0·478	Citric, malic, and succinic	Not ascertained.
21st May, 1890	—	0·516	Ditto	Dextrose, levulose, and inosite.
28th May, 1890....	0·28	0·646	Ditto	Ditto.
10th June, 1890....	1·17	0·656	Malic and citric	Not examined.
19th June, 1890 ...	—	0·739	Ditto	Dextrose, levulose, and traces of inosite.

On the four later dates, the sugar in the leaves was estimated; 0·436, 1·465, 1·321, and 0·813 per cent. respectively being found. This sugar did not reduce Fehling's solution until after inversion. In addition to the vegetable acids above mentioned, crystals of calcium oxalate were seen under the microscope, and traces of formic and acetic acids were obtained by distilling the juice. The distillate from currant juice gave indications of an aldehyde. The progressive increase in the percentage of acid during the whole period is not in harmony with the old view, that the sugar was formed at the expense of the acid. The disappearance of succinic acid, as ripening is approached, suggests the theory that the other acids are formed synthetically from oxalic and succinic acids. The presence of saccharose alone in the leaves (which organs are doubtless the seat of the genesis of the carbohydrates), in proportions which increase as the ripening stage is approached, but subsequently diminish, tends to indicate that the formation of saccharose is the first stage in the production of the sugars, and that the transformation into glucoses in the fruit is effected by the acids there present. No starch was detected at any stage in the fruit itself; the parenchyma cells of the peduncle showed starch granules increasing in amount as the fruit ripened. The ash of the second, third, and fifth samples was analysed with the following results. The portion insoluble in hydrochloric acid was rejected from the analysis.

Ash of Cherries.

			21st May.	28th May.	19th June.
Portion soluble in water.	SiO_2		—	1·510	1·8420
	HCl		0·712	0·424	1·2340
	SO_3		2·934	4·063	3·1800
	P_2O_5		2·509	3·438	5·4034
	Na_2O		1·217	1·331	1·3420
	K_2O		39·459	40·900	44·2090
	CO_2		15·125	14·831	15·3060
Portion soluble in hydrochloric acid.	CaO	ammonia precipitate soluble in acetic acid....	5·578	4·316	2·0003
	MgO		2·774	3·446	3·0876
	P_2O_5		11·907	11·590	8·0174
	Fe_2O_3	ammonia precipitate insoluble in acetic acid...	0·918	1·151	1·6521
	Al_2O_3		2·553	0·800	0·8126
	P_2O_5		4·502	2·018	2·5361
	CaO	not precipitated by ammonia	2·252	3·540	3·1926
	MgO		2·143	1·949	1·5441
	CO_2		4·124	4·919	4·2071
			98·707	100·226	99·5663

Thirteen experiments were conducted on the fermentation of the juice of cherries and red currants, both with and without the addition of yeast, sugar, and water, and the resulting wines were fully analysed. The results are two voluminous for reproduction. The most notable features are the invariable diminution in the amount of acid, which diminution was the more considerable as the fermentation was the more vigorous. In no case did the addition of sugar cause a proportional increase in the glycerol, but merely a comparatively small augmentation. The sugar which escaped fermentation was entirely converted into levulose.

The qualitative results of the action of various reagents on the juice of black and red currants, as well as the characters of their absorption spectra, indicate that the colouring matters of these fruits are closely allied if not identical. Graphic representations of these spectra, as also those of cherries, bilberries, mallows, and phytolacca berries, rosaniline, ponceau, and rocellin are given.

M. J. S.

Chemical Composition of some Leguminous Seeds. By E. Schulze, E. Steiger, and W. Maxwell (*Landw. Versuchs-Stat.*, **39**, 269—326).—*Lupinus luteus.*—After giving the result of the quantitative examination of lupin seeds, the authors give a detailed account of the methods employed in the estimation of the various constituents (compare Schulze and Steiger, *Landw. Versuchs-Stat.*, **36**). The analyses were made with two samples of seeds, freed from skins (1 and 2) and with the skins themselves (3). The following table shows the distribution of the nitrogen percentage in the dry matter :—

	1.	2.	3.
Nitrogen as proteïds (conglutin, legumin, and albumin)	7·86	9·24	0·61
Nitrogen as nucleïn (and plastin ?)	0·10	0·05	0·11
,, non-proteïds	1·24	0·24	0·02
Total nitrogen	9·20	9·53	0·74

In the next table, the percentage composition of the same samples is given, whilst the composition of the entire seeds is shown in the fourth column. These last numbers were obtained by calculation from the result of the other analyses. The seeds contained 26 per cent. of hulls.

	1.	2.	3.	4.
Proteïds	44·48	52·30	3·81	36·79
Nucleïn	0·80	0·40	0·88	0·67
Alkaloïds (lupinine, lupinidine)	1·46	(1·46)	—	1·08
Lecithin	(2·11)	2·16	—	1·58
Cholesterol	0·17	0·18	—	0·13
Glycerides (and free fatty acids)	6·63	5·83	—	4·61
β-Galactan	6·57	10·20	—	7·63
Paragalactan	10·39	8·76	17·91	11·73
Crude fibre	5·21	5·83	54·34	18·21
Soluble organic acids (citric, malic, and oxalic acids)	2·09	2·21	—	1·59
Ether extract (lupeol, &c.)	—	—	0·79	0·21
Soluble carbohydrates	—	—	5·47	—
Ash	4·35	4·27	1·73	3·64
Not determined and loss	15·73	6·40	15·07	12·13

The digestibility of the seeds freed from their skins was determined by Stutzer's method in the powdered seed (freed from fat). The two samples (1 and 2) gave residues containing only 1·09 and 0·53 per cent. of the original total nitrogen. The dry residue (mean) after digestion, was 6·87 per cent. of the dry matter of the shelled seed. It seems probable that the pancreatic extract has no action (or a very slight action) on the paragalactan (compare *Ber.*, **24**, 183).

Vicia sativa, Pisum sativum, and Faba vulgaris.—The seeds were analysed entire. The following table shows the percentage composition of the dry matter :—

	Vicia sativa.	*Pisum sativum.*	*Faba vulgaris.*
Nitrogen as proteïds	4·244	3·583	3·801
„ nucleïn	0·291	0·143	0·239
„ non-proteïds	0·504	0·425	0·435
Total nitrogen	5·039	4·151	4·574
Proteïds	25·46	21·50	22·81
Nucleïn	2·33	1·14	1·91
Lecithin	1·22	1·21	0·81
Cholesterol	0·06	0·06	0·04
Glycerides and free fatty acids	0·91	1·87	1·26
Soluble organic acids (as citric acid)	0·50	0·73	0·88
Cane sugar and galactan	4 85	6·22	4·23
Starch	36·30	40·49	42·66
Crude fibre	4·89	6·03	7·15
Paragalactan and substances not determined	21·60	17·29	15·33
Ash	2·90	3·46	2·92

With regard to digestibility, of 100 parts of nitrogen the residues of the three seeds, after treatment with pancreatic extract, contained respectively 5·77, 3·64, and 5·34 parts. Besides the substances determined, the seeds of *Vicia sativa* contained vicine, convicine, betaïne, cholin, and amygdalin; the seeds of *Pisum sativum* contained cholin and a base similar to betaïne.

Soja hispida.—The seeds contained only a small amount of starch, but more cane sugar than the other seeds. They also contain a considerable amount (1·64 per cent.) of lecithin. N. H. M.

Influence of Iron and Calcium Sulphates on Nitrification. By P. Pichard (*Compt. rend.*, **112**, 1455—1458).—In a pure siliceous sand, kept sufficiently moist and containing unaltered nitrogenous organic matter (cotton oilcake) to the extent of about 1 gram of nitrogen per kilo., the addition of 0·1 per cent. of iron sulphate reduced the loss of nitrogen for seven months from 47·65 to 18·36 per cent., and increased the gain of nitric nitrogen from 1·43 to 10·40 per cent., and that of ammoniacal nitrogen from 4·49 to 11·22 per cent.

With 10 per cent. of clay mixed with the sand, the loss of nitrogen was not sensibly reduced, the gain in nitric nitrogen was increased from 5·10 to 15·92 per cent., and the gain in ammoniacal nitrogen reduced from 16·94 to 12·75 per cent. by the use of the iron sulphate.

Sand containing 1 per cent. of calcium carbonate with iron sulphate did not show any sensible reduction of the loss of nitrogen; the gain of nitric nitrogen diminished from 5·10 to 2·55 per cent., and of ammoniacal nitrogen increased from 6·43 to 10·40 per cent.

In sand containing clay and calcium carbonate, iron sulphate reduced the loss of nitrogen from 31·63 to 23·87 per cent., diminished the gain of nitric nitrogen from 7·14 to 6·43 per cent., and augmented the gain of ammoniacal nitrogen from 18·57 to 26·73 per cent. In the same medium, double and triple allowances of iron sulphate have lessened the loss of nitrogen, gradually diminished the gain of ammoniacal nitrogen, and increased the gain of nitric nitrogen.

Iron sulphate hinders the decomposition of nitrogenous matters, and favours nitrification.

Using iron lactate with a soil containing sand, clay, and calcium carbonate, the iron being in the same proportion as before, loss of nitrogen became 0·20 per cent., gain in nitric nitrogen increased to 22·34 per cent., and gain in ammoniacal nitrogen decreased to 3·57 per cent.

Iron salts appear in general to be detrimental to the ferments destroying nitrogenous matters, but the organic salts of iron favour nitrification.

Ferric oxide added to a complete soil (sandy, clay, and chalk) to the extent of 0·2 per cent. reduced the loss of nitrogen from 31·63 to 21·43 per cent., increased the gain of nitric nitrogen to 19·69 per cent., and reduced the gain of ammoniacal nitrogen to 10·71 per cent. Ferric oxide does not hinder the decomposition of nitrogenous matters; it appears to moderate the energetic action of calcium carbonate, and clearly to favour nitrification, by fixation of ammonia in the same way as clay, and by its oxidising properties.

Calcium sulphate, when introduced to the extent of 0·5 per cent. in the same soils, is found to be superior to iron sulphate in regard to nitrification. In pure siliceous sand, the gain of nitric nitrogen is raised to 11·43 per cent., in sand with chalk to 13·67, in sand with clay to 23·67, and in a complete soil to 34·48 per cent. As a nitrogen preserver, its action is more efficacious than that of iron sulphate, except in the case of siliceous sand, an exception accounted for by its inferior solubility. Calcium sulphate does not retard the decomposition of nitrogenous matters by ferments.

Iron sulphate would be usefully employed to fix ammonia in positions where it is rapidly formed, as in liquid manure ditches, manures, and sewage. Its use would be prejudicial in connection with organic manures which decompose but slowly, on account of its antiseptic properties.

Iron sulphate would be advantageously used as a manure in wet, sandy soils poor in clay, chalk, and ferric oxide. All other soils would be more benefited by the employment of calcium sulphate.

Iron sulphate would be useless, if not detrimental, in the case of ferruginous soils.

Chlorosis due to starving, and not to the influence of meteorological conditions or the ravages of parasites, might be overcome by the use of calcium sulphate as well as iron sulphate.

The practice of adding natural marls containing gypsum is amply justified, as ammonia is fixed by the clay and calcium sulphate, the destruction of nitrogenous organic matter is lessened by the calcium carbonate and the losses of nitrogen diminished, nitrification is rendered regular, and the fixation of atmospheric nitrogen is much promoted. W. T.

Formation and Oxidation of Nitrites in Soils. By S. WINOGRADSKY (*Compt. rend.*, **113**, 89—92; compare Warington, Trans., 1891, 484).—Liquids containing ammonium sulphate and other mineral salts, together with magnesium carbonate, were sown with soils from various parts of the world. In all cases, nitrification started with the formation of nitrites, nitrates not appearing in quantity until the ammonia had disappeared. When, however, successive cultures were made from the soils, the later generations did not preserve the parallelism. With European soils, the formation of nitrates diminished after six or eight generations, and at last ceased; with soil from Quito, nitrites were still being formed after twelve generations; whilst with other South American and African soils, the rate of formation of nitrates was not only maintained, but could be augmented by replenishing the solution with ammonium salts.

In the attenuated cultures, especially in those in which nitrates had been formed, there were observed several kinds of microbes, which bore a general resemblance to the nitrous organism (*nitromonade*). Some of these were isolated, and were found to retain under culture their power of oxidising ammonia, but to lose after a few generations that of oxidising nitrites. An endeavour to isolate the nitric organism from Tunis soil by gelatin culture also gave negative results; but the method by which the nitrous microbe had been isolated proved successful.

A solution of nitrites was sown with Quito soil, and, as soon as the oxidation had become regular, a little drop of the culture was sown in gelatinous silica. Colonies of two different organisms developed, one of which proved to be the nitric microbe. It is a very small, irregular, bent rod, which bears no resemblance to the nitrous organism separated from the same soil. It rapidly converts solution of nitrites into nitrates, but has no action on ammonia.

Organisms of similar function were found in the Java and Zurich soils, and it is probable that, like the nitrous organisms, they constitute a group, of which each soil contains a particular species.

JN. W.

Nitric and Ammoniacal Nitrogen as Manures. By PAGNOUL (*Ann. Agron.*, **17**, 274—283).—Muntz has shown that plants receiving nitrogen only in the form of an ammonium salt can live in a sterilised soil in which nitrification of the ammonia does not take place, and hence concludes that ammonia compounds are directly assimilable by plants; in ordinary soil, well provided with the nitrifying ferments, however, ammonia cannot persist, and plants must nearly always absorb nitrogen as a nitrate.

The author's experiments of 1890 on this point were made in four glass flower pots, holding 2—3 litres, and furnished with tubulures at the bottom, connected by india-rubber tubes to four small flasks. A layer of gravel was placed in each pot, and they were filled with the following media:—

A. Good, arable soil containing, per cent., 0·102 N, 0·098 P_2O_5, 0·290 K_2O, and 1·547 CaO.

B, C, D. Siliceous sand, mixed with 10 grams calcium sulphate.

C received in addition an admixture of 20 grams of the soil A, in order to supply it with the nitrifying ferments.

Similar seeds were sown in the four pots, and A was watered throughout with nothing but pure distilled water. B received at intervals 25 c.c. of a solution containing 100 milligrams N as ammonium sulphate, and 100 milligrams P_2O_5 as superphosphate. C received the same quantities of ammonium sulphate and superphosphate as B, and, in addition, 100 milligrams of potash as potassium chloride in each 25 of nutritive liquid. D received in each 25 c.c. of solution 100 milligrams N as sodium nitrate, and the same quantities of superphosphate and potash salt as C. 20 estimations were made of nitric and ammoniacal nitrogen in the drainage water of each flask at intervals, the nitric nitrogen by a colorimetric process with diphenylamine, and the ammonia by distillation with magnesia and Nesslerising. Nine cuttings of the crops were taken from May 14 to August 22, simultaneously in all the pots, and the total weights obtained were:—

A.	B.	C.	D.
31·7	59·5	106·3	103·1 grams.

Thus the sterile sand, with suitable manures, gave much better yields than the good soil without manure, the organic nitrogen in the latter not being transformed into assimilable compounds with sufficient rapidity. In the presence of soil containing nitrifying ferments, the ammonium sulphate proved as efficacious as its equivalent of sodium nitrate, but the absence of this ferment reduced the yield to one-half.

The results of analyses of the drainage waters on 20 different dates may be summarised thus:—In the drainage of pot A, the barest traces of nitric and ammoniacal nitrogen were found, generally about 0·2 milligram per litre. In that of pot D, which received altogether 1100 milligrams of N as sodium nitrate, mere traces of ammonia were present; nitric nitrogen was found in large quantity (up to 110 milligrams per litre) immediately after each fresh supply of the manurial liquid, but after eight or 10 days, or five or six percolations through the soil, the quantity sank to traces or *nil*, if the plant was in active growth. In the drainage of pot C, nitric and ammoniacal nitrogen were found in something like equal quantities on the whole set of estimations, so that although it is certain much of the ammonia was nitrified, it is not certain whether all the nitrogen that entered the plant was in the form of nitrate. In the drainage of B, large quantities of ammonia were always found, and these increased towards the end of the experiment through accumulation of unused ammonium sulphate; nitric nitrogen was either absent or present in traces only, except towards the end of the experiment, by which time a little nitrifying ferment may have got into the sand. Although the ammonium salt is shown to be far less favourable (in the absence of nitrifying ferments) to the vegetation than the nitrate, the considerable crop obtained renders it extremely probable that some of it was directly assimilated.

Estimations of nitric and ammoniacal nitrogen in the plant itself were made on the cuttings of June 11 and 23 and July 7. The plant from A never contained nitrate, and the merest traces, if any, of ammonia; in that from B, no nitrate was present, but there was a small proportion of ammoniacal nitrogen (13—14 milligrams per 100 grams) on each date; the plants of C and D contained the merest traces, if any, of ammonia, but nitric nitrogen was present in very variable quantity, according to the time which had elapsed since the last supply of nitrogenous manure to the plant; 18 days after, the quantity was 3 and 8 milligrams per 100 grams; seven days after, 140 milligrams per 100 grams. When supplied in abundance, nitrate is first stored in the plant and then its nitrogen is assimilated.

The author's experiments confirm the views of Muntz, already mentioned. J. M. H. M.

Loss of Nitrogen during Decomposition of Nitrogenous Organic Matter, and the Means of Limiting or Avoiding it. By J. H. VOGEL (*Bied. Centr.*, **20**, 562—564; from *J. f. Landw.*, **38**, 327—334).—According to v. Krause (*J. f. Landw.*, **38**, 1), superphosphate is an excellent preservative for manure, and is preferable to superphosphate-gypsum, owing to the greater amount of soluble phosphates it contains. With readily soluble phosphates, there seems to be a gradual formation of calcium carbonate and ammonium phosphate; the free acid takes up the ammonia more quickly, but there remains only a small amount of soluble phosphates which fix ammonia.

The author refutes these views of v. Krause. Small losses of soluble salts cannot be avoided with farm-yard manure. The loss of phosphoric acid is, however, slight, but may be considerable if superphosphate is added to it, so much so that any beneficial action of the superphosphate is more than cancelled. Moreover, the soluble phosphoric acid of the superphosphate, or superphosphate-gypsum, does not combine with the ammonia which is liberated from the farm-yard manure, but mostly goes over into the insoluble state: ammonium sulphate and sparingly soluble calcium phosphates are formed, with merely a trace of ammonium phosphate. The very favourable effect of phosphoric acid in preserving manure is due, in the first place, to its power of so changing the fermentation that no free nitrogen, or but little, is formed. The liberation of nitrogen was shown by Dietzell to be prevented not only by phosphoric acid soluble in water, but also by phosphoric acid soluble in citrate, and the author has already proposed using a preparation which contains, besides calcium and magnesium sulphates, also a large amount of phosphoric acid soluble in citrate.

The loss of free nitrogen, when gypsum is used alone, is not nearly so great as the advantage which follows from the fixation of ammonia.

N. H. M.

Manuring Experiments with Rice. By O. KELLNER, Y. KOZAI, Y. MORI, and M. NAGAOKA (*Landw. Versuchs-Stat.*, **39**, 361—382).—In order to ascertain the food requirements of rice, a number of experiments were made in which rice was grown in soil variously manured. Wagner's method of small plots was employed; these were made by sinking wooden frames, with a surface of nearly a square metre, about 50 cm. into the ground. The air-dried soil (which was of volcanic origin) contained:—Nitrogen, 0·608; phosphoric acid, 0·448; potash, 0·232; and lime, 0·248 per cent. There were five series: the first contained six unmanured plots, three with nitrogen and potash, three with phosphoric acid and potash, and three with phosphoric acid and nitrogen. In the second series, all the plots had the same amounts of phosphoric acid and potash, and varying amounts of nitrogen. In the third series, all the plots had the same amount of nitrogen and potash, and varied amounts of phosphoric acid. In the fourth series, the amounts of nitrogen and phosphoric acid were the same in each case, and the potash varied. In the fifth series, all the plots had nitrogen, phosphoric acid, and potash, and different amounts of lime.

The unmanured plots gave a very poor yield, and the application of much nitrogen and potash alone had no beneficial effect. Phosphoric acid was found to be a most important manure, whilst potash did little or no good. The results showed that, for its full development, rice required a manuring of 7·5 kilos. of nitrogen and 12·5 kilos. of phosphoric acid per one-tenth hectare; in some cases, a small amount of potash is necessary. The usual manuring of the district includes far too little phosphoric acid.

With regard to the effect of the manures on the composition of the crops, it was found that the produce of the unmanured plots, and of those which had nitrogen and potash, was the richest in nitrogen. The produce poorest in nitrogen was obtained from those plots which were manured with much phosphoric acid and potash, but with little or no nitrogen. When much nitrogen was applied, the total dry produce contained more than 1 per cent. of nitrogen, the excess being chiefly in the straw.

The differences in the amounts of phosphoric acid in the produce of the different plots were generally analogous to the difference in the amounts of nitrogen. When no nitrogen, but much phosphoric acid was applied, the straw remained poor in phosphoric acid; this is ascribed to the quick ripening of the plants. N. H. M.

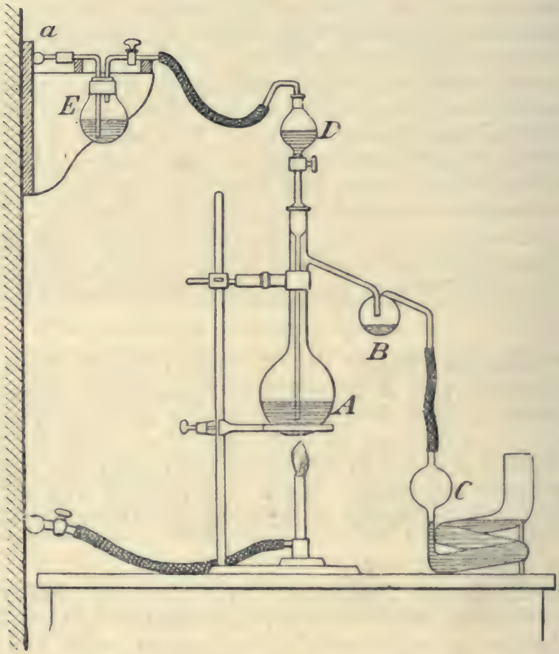
Analytical Chemistry.

The True Litre or Mohr's Litre, for Volumetric Analysis. By W. Fresenius (*Zeit. anal. Chem.*, **30**, 461—465).—The expressed desire that the German Imperial Standards Commission should undertake to test and certify measuring vessels for chemical purposes has brought into prominence the question whether the true litre ought to be used for this purpose, or the very prevalent "Mohr's litre," which is about 2 c.c. greater than the true litre. The Commission, although holding itself bound by the terms of its constitution not to authenticate as a litre measure any vessel which did not conform to the true definition, nevertheless took steps to ascertain the opinions of various scientific men with regard to the question. In view of the common practice of expressing the specific gravities of liquids with reference to water of the same temperature (and that a mean working temperature) as unity, which practice is already recognised by the Commission in testing hydrometers, and considering the convenience of expressing the unit of weight and that of volume by an identical number under practical working conditions, as well as the confusion which would result from neglect of the corrections rendered necessary by the employment of "true" litre vessels at any temperature other than 0°, the author suggests that Mohr's litre should be retained for volumetric work, and that the certificate to be issued should be worded in some such manner as the following:—"The flask X, filled with water of 17·5° C., so far that the mark is tangent to the lower meniscus, contains an amount of water which equipoises a brass kilogram in air of 760 mm. pressure, and therefore holds a so-called Mohr's litre." M. J. S.

Neutral Litmus Paper. By K. MAYS (*Verh. d. Naturhist.-Med. Verein Heidelberg, N.F.*, **3**, 295—298).—An aqueous extract of commercial litmus is acidified with hydrochloric acid, and placed within a parchment paper dialyser for eight days, there being running water outside. Litmus is a colloïd substance, and in this way is freed from saline and other impurities. Paper impregnated with this neutral litmus solution is perfectly satisfactory for the determination of reaction. W. D. H.

Test for Hydrogen Peroxide. By G. DENIGÈS (*Bull. Soc. Chim.* [3], 293).—When a drop of a 10 per cent. solution of metaphenylenediamine chloride is boiled with a few drops of water and a drop of hydrogen peroxide solution, a carmine-red coloration is produced. This reaction will detect 0·005 milligram of hydrogen peroxide in a drop of water, but is affected by the presence of nitrites. The test is thus modified, to be independent of the presence of the latter compounds:—One or two drops of metaphenylenediamine chloride is added to 1 c.c. of ammonia solution containing a few drops of hydrogen peroxide solution; the mixture is boiled for some minutes, when the previously colourless solution becomes blue, of intensity corresponding with the peroxide present; addition of alkali hydroxide solution changes the colour to red. In reference to a former communication (Abstr., 1890, 1185), the author states that the molybdosulphuric acid used for the detection of hydrogen peroxide is made by mixing equal volumes of a recently prepared ammonium molybdate solution (10 per cent.) and concentrated sulphuric acid; the solution, which becomes bluish on keeping, is rendered colourless by warming, and its sensitiveness is unimpaired. T. G. N.

Estimation of Sulphur in Iron. By v. REIS and F. WIGGERT (*Chem. Centr.*, 1891, ii, 218—219; from *Stahl u. Eisen*, **11**, 480—483). —The apparatus employed by the authors is represented in the accompanying figure. *A* is a distillation flask, on the side-tube of which a small bulb *B* is blown, from which a side-tube leads to the absorption apparatus *C*. The stoppered funnel *D* has a ground stopper on the lower limb, which fits the neck of *A*. *E* is a small washing flask for the carbonic anhydride, which is supplied from a cylinder of liquid carbonic anhydride. The absorption liquid consists of equal parts of hydrogen peroxide and dilute (1 : 4) ammonia. The sulphuric acid which may be present in the hydrogen peroxide is previously precipitated *exactly* by the addition of barium chloride, the barium sulphate is allowed to settle, and the clear solution of peroxide siphoned off. *C* should be of such dimensions that 1 litre of gas may be drawn through it in 3·5 minutes.



10 grams of the iron or steel is introduced into *A*, the tap of *D* opened, and carbonic anhydride allowed to flow into the apparatus, which forces the hydrochloric acid from the funnel into the flask, after which the tap of *D* is again closed. In the case of steel, a small flame may be at once applied to the flask *A*; for iron 2—3 minutes should be allowed to elapse before heating. In about 5 minutes, the liquid is brought to boiling, and carbonic anhydride is then allowed to flow rapidly through the apparatus for 20 minutes.

The contents of *C* are now transferred to a beaker, and *C* is rinsed with 100 c.c. of water, the total volume now measuring 200 c.c. It is boiled for 2—3 minutes, 10 c.c. of dilute 1 : 1-hydrochloric acid added, and boiled again to expel all carbonic anhydride. 10 c.c. of ammonia, sp. gr. 0·96, is added, together with 2 or 3 drops of methyl-orange, and if the liquid should still be acid, a little more ammonia is added, and the liquid is now neutralised very carefully with hydrochloric acid, so that the methyl-orange is not red, but only orange-coloured. It is now heated to boiling, 10 c.c. of barium nitrate solution (70 grams in 1000 c.c.) added, again heated to boiling, 10 c.c. of dilute hydrochloric acid added, and the precipitate allowed to settle while warm. After 15 minutes, it is collected, washed with hydrochloric acid and water, and the filter is placed in a porcelain crucible, charred in a muffle, and ignited for 15 minutes at a red heat. The whole determination lasts about two hours. The authors have found that the barium sulphate, if precipitated with barium nitrate from an exactly neutral liquid, and in the absence of metals, is very dense and easily filtered. The use of a mechanical stirrer still further shortens the time.

J. W. L.

Sulphuric Acid in Plastered and Natural Wines. By D. VITALI (*L'Orosi*, **14**, 145—163).—Roos and Thomas (*Compt. rend.*, **111**, 575) concluded that plastered wines contain normal potassium sulphate, because on adding ammonium acetate to the wine, precipitating the sulphuric acid with barium chloride, and igniting, the whole of the chlorine is found in the residue, whereas if an acid sulphate were present, some of the chlorine would be volatilised as ammonium chloride. The author finds, however, that under the above conditions ammonium chloride reacts with the potassium and calcium tartrates in the wine, so that the whole of the chlorine is fixed and remains in the ash.

The presence of acid sulphates in plastered wines may be demonstrated by treating them with some alkaloïd, such as quinidine, which is capable of extracting sulphuric acid from potassium hydrogen sulphate but has no action on the normal salt. The experiment is conducted as follows: an excess of freshly precipitated quinidine is added to the wine (3 parts) until its red colour is changed to a violet-blue, the whole briskly shaken, heated for a short time at 50—60°, chloroform (2 vols.), and sufficient absolute alcohol to dissolve it added, and then, without shaking, a volume of water about half the volume of the mixture is also added. After a time, the clear chloroform solution is drawn off, evaporated, and the residue tested for sulphuric acid. By the above method, the author has also succeeded in proving the presence of acid sulphates in the urine.

The presence of nitric acid in wine may also be detected by treating it with quinidine as above, evaporating the chloroform solution, treating the residue with water and potassium carbonate, to convert the nitric acid into potassium nitrate; this remains undissolved on treating the mass with alcohol and chloroform, and may be identified by the ordinary methods.

S. B. A. A.

Estimation of Small Quantities of Boric Acid. By F. PARMENTIER (*Compt. rend.*, **113**, 41—43).—The method is based on the difference in the behaviour of helianthin and litmus or orceïn towards boric acid and its salts. Yellow (alkaline) helianthin is not affected by boric acid or borates, whilst alkaline litmus, or, better, orceïn, changes colour when the base is partially or entirely saturated. When the alkali is soda, the point is that at which the biborate is formed.

To estimate the boric acid in a mineral water, the residue, after removal of the silica, is dissolved in hydrochloric acid, and treated with ammonium nitrate and ammonia, to precipitate the iron, alumina, manganese, and arsenic and phosphoric acids. The filtrate is then acidified with hydrochloric acid, and divided into two equal portions, both of which are titrated with sodium carbonate, one with helianthin as indicator, the other with orceïn.

In this way quantities of boric anhydride as minute as 1·8—3·8 milligrams per litre have been found in the waters of Royat.

Jn. W.

Detection of Carbonic Oxide in Blood. By H. Bertin-Sans and J. Moitessier (*Compt. rend.*, **113**, 210—211).—See this vol., p. 1522.

Separation of Barium from Calcium. By R. Fresenius (*Zeit. anal. Chem.*, **30**, 452—460).—When a solution containing much calcium with little barium, and feebly acidified with hydrochloric acid, is precipitated with a quantity of sulphuric acid only a little greater than is required to form barium sulphate with the barium present, the whole of the barium is not precipitated, although the precipitate retains some calcium, even after washing until calcium is no longer to be detected in the washings. If, on the other hand, six times as much sulphuric acid is added as corresponds with the barium present, the whole of the barium is indeed precipitated, but calcium is also thrown down, even when the amount of water present is nearly double that required to hold all the calcium sulphate in solution. In presence of a large quantity of hydrochloric acid, barium can be precipitated with approximate completeness only when much sulphuric acid is added. Thus, 400,000 parts of a liquid containing 1·2 per cent. of hydrogen chloride and 0·38 per cent. of sulphuric anhydride was required to dissolve 1 part of barium sulphate, whilst with the same strength of hydrochloric acid, but with sulphuric acid only slightly in excess of the barium present, the solubility was 1 part in 18,000. With a large excess of both hydrochloric and sulphuric acids, the separation of barium and calcium seems at first to be accurate, and is, in fact, better than with feebly acid liquids; it is, however, still imperfect. Diehl's method of separating the two bases, by digesting the mixed sulphates with a concentrated solution of sodium thiosulphate, gives approximately accurate results when the two sulphates have been precipitated separately and then mixed, though a little barium is lost, since barium sulphate is not absolutely insoluble in strong thiosulphate solution. When applied, however, to the sulphates precipitated simultaneously, a considerable amount of calcium sulphate remains undissolved. It is further to be noticed that from a thiosulphate solution, calcium cannot be completely precipitated by ammonium oxalate. M. J. S.

Electrolytic Estimation of Metals as Amalgams. By G. VORTMANN (*Ber.*, **24**, 2749—2765).—The metals are best obtained in the form of amalgams, by adding to the solution the corresponding salt to be examined, and a weighed quantity of mercuric chloride; in the case of acid solutions, pure precipitated mercuric oxide may be employed. At the commencement of the operation, a current giving 6—8 c.c. of oxyhydrogen gas per minute is employed; when the metal begins to be deposited, this is reduced to one giving 2—3 c.c., and, as the analysis proceeds, the current is gradually increased to its original strength. Mercury alone is quantitatively precipitated by electrolysis from solutions containing ammonium oxalate, ammonium tartrate, or alkaline sodium sulphide. After the deposition of mercury from solution in potassium iodide, it is needful to dissolve the iodine deposited on the positive electrode in soda and continue the electrolysis for an hour, or if the quantity of iodine is very small, it may be sufficient to wash the metal quickly with sodium sulphite solution. Mercury can also be deposited from an alkaline solution of potassium mercuric iodide; in this case, the metal should not be washed with alcohol, or particles will become detached.

Zinc is best deposited from solutions containing ammonium oxalate or from ammoniacal solutions; in the first case, not more than 2—3 parts of mercury should be added for 1 of zinc, but in the latter solution, the proportion should be at least 3 parts of mercury to 1 of zinc. As the platinum vessel is attacked during the operation, it is advisable either to deposit the zinc directly and not as an amalgam, or to employ a dish coated with copper or silver.

The determination of cadmium resembles that of zinc; on account of the sparing solubility of cadmium oxalate, it is best to employ an ammoniacal solution, unless the quantity of cadmium does not exceed 0·2—0·3 gram; there should be 4—6 parts of mercury to 1 of cadmium.

The deposition of lead from acid solutions is effected by dissolving the lead salt, together with mercuric chloride, in water, adding sodium acetate and a little concentrated potassium nitrite solution, the resulting precipitate being dissolved by the addition of acetic acid; the formation of any lead oxide towards the end of the operation can be prevented by the addition of small quantities of potassium nitrite. The lead amalgam is stable when dry, but in presence of moisture is quickly oxidised on exposure to air. Lead is also deposited quantitatively from alkaline solution; as the use of alcohol to dry the amalgam would cause loss, oxidation takes place, and consequently the results are somewhat high. The method affords, however, a ready means of separating lead from other metals, such as tin, antimony, or arsenic, and for this purpose it is convenient to employ an ammoniacal solution containing tartaric acid; when all the lead is deposited, the supernatant liquor is poured off, the amalgam dissolved in acid, and the solution treated as above described.

Bismuth is best determined in hydrochloric acid solution, the precipitation of basic salts being prevented by the addition of excess of potassium iodide, or by dilution with ethyl alcohol mixed with 2 parts of water. The second method is much better if bismuth is present. The amalgam is stable, and may be heated at 90° in an air-bath without suffering any change. Should the bismuth be dissolved in nitric acid, not less than 4 parts of mercury to 1 of bismuth should be present, and it is necessary to add tartaric acid. The quantitative deposition of bismuth from ammoniacal solutions containing tartaric acid is unsatisfactory, but affords a useful means of separating it from tin, antimony, and arsenic.

Antimony is first oxidised to antimonic anhydride and then dissolved in soda and sodium sulphide; 2 parts of mercury to 1 of antimony must be present. The amalgam is very stable. As antimony is not precipitated from ammoniacal solutions containing ammonium tartrate, such a solution may be used to separate it from lead and other metals, whilst the first method enables it to be separated from tin.

No means have yet been discovered of determining arsenic in the form of its amalgam; during electrolysis, considerable quantities of arsenic hydride are evolved, and hitherto attempts to decompose this at the moment of its formation have proved fruitless. Arsenic amalgam undergoes no change on exposure to the air. J. B. T.

Antimony Pentasulphide: Separation of Arsenic and Antimony. By T. Wilm (*Zeit. anal. Chem.*, **30**, 428—446).—See this vol., p. 1432.

Detection and Separation of Metals of the Platinum Group in presence of other Metals. By A. Joly and E. Leidié (*Compt. rend.*, **112**, 1259—1261).—Osmium and ruthenium are removed in the form of volatile compounds, and iridium is removed by treatment with lead. A moderately dilute hydrochloric acid solution of the remaining metals is heated to about 60° and mixed with potassium nitrite. If much platinum is present, potassium platinochloride gradually separates as a crystalline precipitate quite free from other metals. After cooling and separation of this salt, the liquid is again heated and further quantities of nitrite added. Suddenly, and especially if the liquid is stirred, the crystalline double rhodium compound separates, carrying with it lead, bismuth, and tin, and small quantities of copper. If the liquid is allowed to cool, the separation of the rhodium becomes complete, provided that a moderately large quantity of potassium chloride is present. Should iron and copper be present, the addition of the nitrite is continued until the liquid becomes alkaline, and, on boiling, the iron and copper are precipitated, whilst platinum and palladium remain in solution. C. H. B.

Water Analysis. By C. Lepierre (*Bull. Soc. Chim.* [3], **5**, 299—307).—A criticism of Boutron and Boudet's method for estimating hardness. The author describes the preparation of standard almond oil soap solution such that 1 c.c. corresponds with 1 milligram of dissolved calcium chloride, and records experiments and the calculated equivalent values for other calcium and magnesium compounds. Contrary to Wanklyn and Chapman, he states that magnesian waters do not require $1\frac{1}{2}$ times their calculated equivalent of soap solution for complete precipitation, but that the amounts required are the same as with calcium solutions of equivalent strength. It is only with solutions containing between 20 and 30 grams of calcium chloride (or its equivalent in other calcium or magnesium salts) per litre that the soap solution required is directly proportional; both weaker and stronger solutions require relatively more soap solution. Tables are given for calcium salts and magnesium salts. T. G. N.

Detection of Cyanogen Compounds. By A. Hilger and K. Tamba (*Zeit. anal. Chem.*, **30**, 529; from *Mittheil. aus dem pharm. Inst. der Univers. Erlangen*, Heft ii).—Guaiacum-copper sulphate paper is a very untrustworthy test. It is much better to add to the suspected distillate in a basin a drop of freshly made guaiacum tincture and then a drop of copper sulphate. To detect cyanides in presence of ferrocyanides, the substance should be mixed with tartaric acid, then gradually made feebly alkaline with sodium carbonate, and treated with a current of carbonic anhydride in a distillation apparatus at a temperature not exceeding 60°, and the distillate tested. All metallic cyanogen compounds are decomposed by carbonic anhydride at 100°; but ferrocyanides and ferricyanides not below 80°, whilst the simple cyanides, including mercuric cyanide, are decomposed between 50° and 60°. M. J. S.

Detection of Turkish Geranium Essence in Oil of Roses. By G. Panafotow (*Ber.*, **24**, 2700—2701).—Oil of roses from South Bulgaria and Turkey is very often adulterated with Turkish geranium essence (*Indris Yaghi*); the presence of even traces of the latter can, however, be easily detected, since a mixture (2 to 3 drops) of the two oils gives a blue coloration on shaking with a solution of rosaniline previously decolorised with sulphurous anhydride, and then keeping for about two hours. Pure oil of roses gives a red coloration after shaking with the reagent and then keeping for about 24 hours.

When Turkish geranium essence is mixed with an equal quantity of concentrated sulphuric acid on a watch glass, a considerable development of heat occurs, and dense, white fumes, having a tarry odour, are evolved; on adding 95 per cent. alcohol to the brownish-red mixture, a yellow, fatty, flocculent substance is precipitated, and the solution, which is at first red, changes to yellow on keeping for some time. Oil of roses also gives, with concentrated sulphuric acid, a brownish-red solution, but, on the addition of alcohol, a clear, almost colourless solution is obtained. This difference in behaviour can also be made use of for the detection of geranium essence in oil of roses.

F. S. K.

Estimation of the Impurities in Alcohol by Röse's Method. By A. Scala (*Gazzetta*, **21**, 346—374).—The author gives a summary of our knowledge of the impurities present in commercial spirits, and then details experiments made to determine the trustworthiness of Röse's method of estimating the quantity of fusel oil present.

The experiments on the increase of volume experienced by chloroform, when agitated with spirit containing amyl alcohol or other ordinary impurities, are carried out in a stoppered glass cylinder of the form usually employed, having a capacity of 150 c.c., and a scale graduated in twentieths of a c.c. This is washed first with concentrated sulphuric acid, then with nitric acid, and finally with water, and well dried; a little more than 20 c.c. of carefully purified chloroform is then put in, by means of a long-stemmed funnel, and the cylinder left in a bath until it has attained a temperature of 15°; the excess of chloroform is now taken out, leaving exactly 20 c.c. Meanwhile, pure alcohol has been diluted to a strength of 30 vols. per cent., the required quantity of impurity added, and the strength again reduced to 30 vols. per cent. by addition of water or alcohol; 100 c.c. of this spirit is now put into the cylinder, together with 1 c.c. of sulphuric acid of density 1·286, all being kept at the standard temperature. After well agitating, the cylinder is returned to the bath, and the volume of the chloroform read off after 20 minutes.

The unit, from which the augmentation in volume of the chloroform is to be calculated, is obtained by performing the test with pure dilute alcohol of the standard strength, namely, 30 vols. per cent., and is 21·59 at the standard temperature. Consequently, this number must be subtracted from the volume obtained when operating with an impure spirit, in order to obtain the increase in volume due to the impurity.

A variation of ± 1 vol. per cent. in the strength of the alcohol employed is attended by a variation of ±0·26 c.c. in the volume of chloroform obtained. A rise of temperature of 1° increases the volume of chloroform by 0·036 c.c. on the volume at 15°, but if the unit volume, that is to say, the volume which 20 c.c. of chloroform occupies after agitation with 100 c.c. of 30 vols. per cent. alcohol, be determined at temperatures other than 15°, the increase in volume due to fusel oil is practically a constant for other temperatures.

The results of an examination of the effect on the volume of the chloroform of other substances which might occur in spirits are embodied in the following table. The numbers give the increase in volume, over and above the unit volume, due to the presence of 1 c.c. of the corresponding substance in each 100 c.c. of 30 vols. per cent. spirit.

Name of substance.	Increase in volume.
Acetaldehyde	0·200 c.c.
Paraldehyde	1·000 ,,
Furfuraldehyde	0·601 ,,
Propyl alcohol	0·502 ,,
Normal butyl alcohol	1·161 ,,
Isobutyl alcohol	0·949 ,,
Amyl alcohol	1·507 ,,
Essence of aniseed	0·588 ,,
,, cinnamon	0·750 ,,

In the case of furfuraldehyde, there is seemingly a discrepancy between the values given in the table and in the text.

The increase in volume of the chloroform is directly proportional to the quantity of fusel oil present, and the author gives a table obtained by interpolation, from which the quantity present is deduced directly from that increase.

By previous distillation of the spirit with a few drops of potash, most of the acetaldehyde and furfuraldehyde is retained by the potash, but the proportions of the other impurities present are practically unaltered by this treatment.

The author considers that this method for the determination of fusel oil is quite satisfactory if employed with the precautions detailed above, but that its indications are not to be depended on in the case of those liquors of which aromatic essences in quantity are essential constituents. W. J. P.

Estimation of Phenol. By L. Carré (*Compt. rend.*, **113**, 139—141).—10 grams of pure phenol is dissolved in 1000 c.c. of water, and from this solutions are prepared containing 5·0, 3·0, 2·0, 1·0, 0·8, 0·6, 0·4, 0·2, and 0·1 gram of phenol per litre.

The phenol solution to be examined, if concentrated, is diluted with 10 times its volume of water. 25 c.c. of the solution is placed in a conical flask with 5 c.c. of nitric acid, and equal quantities of the standard solutions of phenol are treated in a similar manner, all the flasks being heated in the same water-bath for one or two hours. The intensity of the coloration produced is proportional to the quantity of phenol present. Greater accuracy is obtained if, after the action has ceased, the solutions are mixed with 20 c.c. of sodium hydroxide solution and diluted to exactly 50 c.c. The liquids are filtered, and compared by means of the colorimeter.

If alcohol is present, the action of heat must be continued until all the alcohol has been expelled; if the quantity of alcohol is considerable, the liquid must be diluted, in order to avoid the formation of ethyl nitrite. In the case of impure phenol, the heating must be continued until all tarry products are destroyed. As a rule, the termination of the reaction is indicated by the disappearance of the turbidity that was produced by the addition of the nitric acid. C. H. B.

Estimation of Sugar and Tannin in Wines. By J. H. Vogel (*Zeit. ang. Chem.*, 1891, 44—69).—The author has proved by several experiments that it is absolutely necessary to first remove the tannin and colouring matters before attempting to estimate the sugars by Fehling's solution. 25 c.c. of a 1 per cent. solution of tannin gave an amount of metallic copper corresponding with 0·91 per cent. of sugar. As the amount of tannin in Portuguese wines often is as high as 3 per cent., the importance of fully removing the tannin will be readily understood. After a short treatment with an insufficient amount of animal charcoal, the tannin is removed before the colouring matters are precipitated, and this fact enabled the author to prove that these colouring matters exercise a powerful reduction on the Fehling's solution, as the yield of copper became greater as the solution was more coloured. Their removal is best effected either with animal charcoal or basic lead acetate, but the author has made several important observations. As to the use of lead solution, 3 c.c. is supposed to be sufficient for 60 c.c. of Rhine wine, whilst for red wines, the amount must be doubled. But in the case of Portuguese wines, this amount is far too small, and the author has met with a sample which required three times its bulk of *liquor plumbi* before it was completely decolorised. The excess of lead must be removed, according to Barth, by sodium carbonate, but the lead separates slowly, causing afterwards an increase in the weight of the copper precipitate, and unless the filtration has been very carefully effected, the sugar may come out from 0·2 to 2·2 per cent. too high, the error increasing with the amount of lead solution used. For wines rich in tannin and colouring matters, the charcoal process is the best. If, for this purpose, powdered purified animal charcoal is used, 25 grams of the charcoal will be found sufficient for 200 c.c. of wine. The time the charcoal is allowed to act varies from 15 to 60 minutes, according to the amount of colouring matters present. A little sugar is also absorbed by the charcoal, but the author, who has thoroughly investigated the matter, finds the amount never to exceed 0·3 per cent. under the most unfavourable conditions. In some cases, it is advisable to first dilute the sample with a known volume of water before attempting to decolorise with the charcoal. The author next investigated the two chief processes used for the estimation of the tannin. It must be borne in mind that this acid, as it occurs in wines, is not at all a definite chemical compound, and is not identical with gallo-tannic acid. The percentage found by analysis is therefore not the true one, but only expresses its equivalent in gallo-tannic acid. The process which was found to answer best was that of Löwenthal. According to this method, the solution containing the tannin is largely diluted with water, mixed with a definite quantity of solution of indigo carmine, containing sulphuric acid, and then titrated with a weak solution of potassium permanganate. Operating on a known quantity of tannin, and deducting the permanganate necessary for the oxidation of the indigo alone, the exact strength of the permanganate expressed in tannin is of course obtained.

In applying the process to wine, which of course contains many other organic matters, also oxidisable by permanganate, the author proceeds as follows: 20 c.c. of the sample is mixed with 2 litres of rainwater, 20 c.c. of solution of indigo-carmine (30 grams per litre), and 10 c.c. of sulphuric acid. A solution of potassium permanganate (1 : 1000) which has been carefully standardised is now run in until the liquid just loses its green, and changes to a bright-yellow, colour. To obtain the amount of permanganate absorbed by the organic matter, 50 c.c. of the sample is mixed with 100 c.c. of a solution of gelatin (1 : 1000), and 60 c.c. (= 20 c.c. of original sample) is filtered off, and again titrated. The difference between the two titrations represents the true amount of tannin. The permanganate absorbed by the excess of the gelatin varies but slightly, but may be put down as 0·2 c.c. As regards the process depending on the precipitation of the tannin by an ammoniacal solution of zinc acetate, previous to titration, the author found it to give results far too high and generally untrustworthy, even with solutions of pure tannic acid.

L. DE K.

Estimation of Cane Sugar in Soap. By J. A. WILSON (*Chem. News*, **64**, 28—29).—The following method is found to be satisfactory :—A saturated solution of magnesium sulphate is gradually added and stirred into 10 grams of soap dissolved in 150 c.c. of water at 80°, and the magnesium soap is washed on a filter with hot water containing a small quantity of magnesium sulphate. The filtrate and washings, after almost neutralising with dilute nitric acid, are evaporated to 40 c.c., and, when cool, acidified with dilute nitric acid, treated with a few drops of basic lead acetate and 2 c.c. of alumina emulsion, diluted to 50 c.c., and the solution polarised in a 200 mm. tube.

D. A. L.

Examination of Urine for Sugar. By E. Luther (*Chem. Centr.*, 1891, ii, 90—91; from *Centr. med. Wiss.*, 1891, 357—358).—The author has employed Molisch's furfuraldehyde reaction, as improved by Udranszky, for determining the sugar in urines (Abstr., 1888, 863, 878).

He finds that a 0·1 per cent. solution of sugar gives the colour reaction and spectrum immediately; a 0·2 per cent. solution gives the coloration faintly after shaking several times, the violet colour passing later into a red.

One drop of the undiluted urine is first tested, and if it gives the furfuraldehyde reaction, it is diluted until the lowest limit, representing a 0·02 per cent. solution, of sugar is reached, from which the amount of sugar present may be calculated.

The naphthol test only indicates, however, the presence of carbohydrates generally, and, since gum is present in urines, the author makes a second determination after allowing the sugar to ferment with yeast, the difference between the total carbohydrates and the gum being grape sugar. In the case of diabetic urines, the amount of sugar, as determined by this method, is higher than if determined by either titration or polarisation. From a large number of determinations of sugar in urines, the author concludes that grape sugar is present in all urine, the amount found in that of adult persons being about 0·1 per cent., and varies according to the quality and quantity of the food, and depends also on the length of time which has elapsed since the meal. The total carbohydrates amount to 0·2 per cent. The kidneys possess the power of allowing sugar to pass in a slight degree, which is increased by those circumstances which cause an increase in the amount of sugar in the blood. It is for this reason that the urine of lying-in women contains relatively more milk sugar than usual.

J. W. L.

Babcock Method for Estimating Fat in Milk. By F. T. Shutt (*Chem. News*, **64**, 3—4).—In the author's hands, the Babcock method for estimating fat in milk yielded fairly accordant results in duplicate experiments; but, in comparison with gravimetric analysis, the results were somewhat low; the maximum deficit recorded is, however, 0·25 per cent. In applying the method, the sulphuric acid is added to, and well mixed with, the milk, and, while still hot, the mixture is centrifugalised in the machine, which is also kept hot with hot water. Hot water is then added, and the amount of fat noted immediately at the close of the operation.

D. A. L.

Reactions of Olive Oil. By G. de Negri and G. Fabris (*Chem. Centr.*, 1891, ii, 87—88).—After an exhaustive examination of a large number of samples of olive oil of known purity, the authors find (*a*) the iodine "number" is slightly higher for oils derived from mature than from immature olives, whilst the reverse is the case with regard to the age of the oil; also, the mode of manufacture has an influence on this test. On the other hand, the locality of growth has no influence on the iodine test, whilst the variety of olive influences the iodine-absorbing quality of the oil, and the "number" rises to 88 in some cases. The specific gravity is almost constant, varying only from 0·916 to 0·918 at 15°. The free fatty acid of the oil melts at 24—27° and solidifies at 17—22°, the determinations being made with samples obtained by pressing the olive; the fatty acids of oil obtained by extracting the olives with carbon bisulphide or ether melt at 25—29° and solidify at 22°. The "saturation equivalent" (milligrams of KHO required to saponify 1 gram of oil) varies from 185 to 196, and is 190 for most samples. The temperature of a mixture of olive oil and concentrated sulphuric acid was nearly constant at 35°, the lowest reading being 32° and the highest 37°. The pure oil does not give any peculiar colorations with those reagents which are usually employed for distinguishing oils; those oils, however, which are obtained from immature olives, or which are extracted by carbon bisulphide, give colour reactions of an indefinite character

J. W. L.

Estimation of Fatty Matter in Turkey-red Oil (Oleïne). By R. WILLIAMS (*Chem. News*, **64**, 15—16).—The volumetric method, heating with dilute acid and some salt solution on the water-bath, adding more hot salt solution, and then reading the volume of fat when cold, gives results 2 to 4 per cent. too high, whereas low results are obtained by the Wilson method, in which the oil mixed with brine and hydrochloric acid is extracted twice with ether, the mixed extracts evaporated, and the residue dried by means of dry air, absolute alcohol, and heating. The author has obtained satisfactory results with the wax method in the following manner:—200 grains of the sample is warmed with 50 grains of 10 per cent. hydrochloric acid and 300 grains of saturated salt solution, warmed gently for a few minutes, 200 grains of wax added, and the whole heated until perfectly liquid. After cooling for some hours, the cake of wax is removed, washed with saturated salt solution, then with a little cold water, dried first with filter paper, then either over sulphuric acid in a desiccator or by heating not above 160° F. and stirring. The weight, less dish and wax, gives the quantity of fat. D. A. L.

Lard and its Adulterations. By H. W. WILEY (*Zeit. anal. Chem.*, **30**, 510—516; from *Foods and Food Adulterants, Washington Government Printing Office*, 1889).—The specific gravity of pure lard is about 0·89 at 40° and about 0·86 at 100°, referred to water of 4°. According to the part of the body from which the fat is taken, the melting point may vary from 35·1° to 44°, and the iodine absorption from 52·55 to 85·03 per cent. The chief adulterants are beef tallow and cotton-seed oil. Bechi's silver nitrate test, Maumené's sulphuric acid reaction (Abstr., 1889, 319, 320), and the microscopic examination of the crystals from ethereal solution (Abstr., 1890, 428) are all recommended. The author's method of determining the melting point of a fat is described, and the apparatus figured (compare Abstr., 1888, 93). M. J. S.

Estimation of Urea. By K. A. H. Mörner and J. Sjöquist (*Chem. Centr.*, 1891, ii, 230—231, from *Centr. Physiol.*, **5**, 150—152). —To 5 c.c. of the urine in a flask, 5 c.c. of a saturated solution of barium chloride containing 5 per cent. of barium hydroxide is added also 100 c.c. of ether-alcohol (2 parts of 97 per cent. alcohol to 1 part of ether), and the mixture is allowed to remain in the closed flask until the following day; the precipitate is filtered off and washed with ether-alcohol. The ether-alcohol is separated from the filtrate at a temperature of 55° (not exceeding 60°), by means of a current of air at low pressure being passed through the liquid. When the volume is reduced to 25 c.c., a little water and some magnesia are added, and the evaporation continued until the distillate shows no alkaline reaction. The residual liquid, measuring from 15—20 c.c., is treated with a few drops of concentrated sulphuric acid and evaporated on the water-bath, after which the nitrogen in it is determined by Kjeldahl's method and calculated into urea. J. W. L.

Reactions of Cocaïne and of Ecgonine. By D. Vitali *L'Orosi*, **14**, 1—19).—If a barely visible particle of cocaïne is placed in a porcelain capsule, covered with 0·5 to 1 c.c. of concentrated sulphuric acid, stirred until solution is complete, and a quantity of potassium or sodium iodate or iodic acid twice or three times as great as that of the cocaïne taken is added, and the whole gently heated with great care on the water-bath, the liquid soon exhibits striations of a bright green colour, which, on continued heating, changes to grass-green, and subsequently into blue; on raising the temperature, the liquid becomes violet, and violet fumes are evolved. This reaction is very sensitive, and is obtained very clearly with 0·00005 gram of the hydrochloride; with very careful working, 0·00002 gram of the base may be recognised. The action of sulphuric and iodic acids on a large number of alkaloïds has been investigated by the author, and from the results, which are given at length, it appears that whilst many alkaloïds, as for example, thebaïne, atropine, chelidonine, coridaline, &c., exhibit highly characteristic colour changes, only caffeïne and theobromine give the same sequence of chromatic effects when the test is made as described for cocaïne. If, however, the quantity of iodic acid used is not too small, the greenish or bluish-green coloration exhibited by these alkaloïds is not followed by any violet coloration, as in the case of cocaïne. Traces of benzoic acid behave with sulphuric and iodic acids exactly like cocaïne, and the behaviour of the alkaloïd is probably due to its decomposition by sulphuric acid with the formation of some benzoic acid. Ecgonine gives under the same conditions a yellow coloration, which quickly changes to bright red, and finally to brown.

On adding a drop or two of a dilute sulphuric acid solution of potassium permanganate (0·5 per cent.) to a little cocaïne dissolved in a few c.c. of concentrated sulphuric acid, a violet coloration is obtained which disappears on agitation, and reappears on adding more of the reagent. With ecgonine, a yellow coloration is given by the first few drops of the reagent, and subsequent additions produce a violet coloration, which is more stable than that obtained with cocaïne.

A solution of iodine in potassium iodide affords a ready means of distinguishing cocaïne from ecgonine. With the former, a reddish-brown precipitate is formed, consisting of microscopic, perfectly spherical, black globules; ecgonine likewise yields a reddish-brown precipitate, which, however, becomes crystalline in a few minutes, forming microscopic tufts of reddish-yellow, rhombic tables or prisms. No crystallisation is obtained if the dilution of the solution is more than 500 to 1. Ecgonine may be recognised by this test in the extracts from animal remains; urine must, however, be tested directly by placing a drop on a glass slip, adding one or two drops of the reagent, allowing it to evaporate almost to dryness, and examining under the microscope. The urine must contain at least 1/600 of ecgonine. From further experiments made by the author, it appears that cocaïne is not affected by prolonged contact with putrefying animal remains, and that, when taken internally, it is almost entirely decomposed within the system, only a very small proportion passing into the urine. S. B. A. A.

Ammonium Selenite as a Reagent for Alkaloïds. By A. J. Ferreira da Silva (*Compt. rend.*, **112**, 1266—1268).—The reagent is prepared by dissolving 1 gram of ammonium selenite in 20 c.c. of concentrated sulphuric acid.

Atropine, no coloration. *Aconitine*, no immediate change; after 20 minutes, very slight rose coloration. *Berberine*, greenish-yellow coloration, becoming very brown, then rose at the edges and violet in the middle, and after half an hour wine-red, persisting for three hours. *Brucine*, rose or reddish coloration, becoming pale-orange; after half an hour, amber colour with no precipitate; no further change. *Caffeïne*, no coloration; after three hours, reddish tint and slight precipitate. *Cinchonidine*, no reaction. *Cinchonine*, no reaction. *Cocaïne*, no perceptible coloration or precipitate after half an hour; after three hours, same result as with caffeïne. *Curarine*, slight violet coloration, becoming reddish after some time; no precipitate after three hours. *Delphine*, slightly reddish coloration, changing to violet-red; no precipitate after three hours. *Digitaline*, no immediate coloration; after half an hour, yellowish; after three hours, reddish precipitate. *Eserine*, lemon-yellow coloration, becoming orange; paler after three hours. *Morphine*, very bright greenish-blue coloration; after half an hour, yellowish-maroon, with no precipitate; after three hours, brown-maroon, with no precipitate. *Narcotine*, bluish coloration, becoming violet and afterwards reddish; after half an hour, beautiful reddish colour, and no precipitate; after three hours, slight red precipitate. *Narceïne*, yellowish-green coloration, becoming brownish, and, after half an hour, reddish; distinct red precipitate after two or three hours. *Papaverine*, bluish coloration, becoming bottle-green, dull yellowish-green, blue-violet, and finally red; slight bluish precipitate. *Pilocarpine*, no reaction. *Solanine*, canary-yellow, changing to brown; after half an hour, a rose ring; after three hours, red-violet. *Saponine*, yellowish coloration, becoming reddish; indistinct reaction. *Senegine*, slight dull-yellow coloration; after three hours, reddish. *Veratrine*, indistinct yellowish coloration, sometimes with a green tinge, becoming yellow after half an hour; after three hours, red precipitate and indistinct yellowish liquid.

The colorations and precipitates are not due merely to the reducing power of the alkaloïds, as Lafon supposes, for narceïne produces a much more rapid precipitation of selenium than does morphine, although the latter is the more powerful reducing agent of the two.

C. H. B.

Extraction of the Colouring Matter of Wines. By L. Hugounenq (*J. Pharm.* [5], **24**, 51—53).—A 10 per cent. solution of tartaric acid is neutralised with a slight excess of ammonia; to this is added normal lead acetate until the lead precipitate just begins to be permanent. After a time, this solution is filtered and added to the wine, previously neutralised by ammonia, as long as a precipitate forms. This precipitate is washed, suspended in a small quantity of 80° alcohol, and a 15 per cent. solution of sulphuric acid added drop by drop, excess being avoided. The solution takes an intense red colour, and lead sulphate is precipitated, which is filtered off after some hours. To the alcoholic solution is added about 20 times its volume of water, when almost the whole of the colouring matter is precipitated; this is collected, washed, and dried at a low temperature. To purify the product, it is dissolved in alcohol, and evaporated in a vacuum over sulphuric acid. The colouring matter of berries and flowers used to falsify wine can also be isolated by this method.

J. T.

Method of Detecting Artificial Coloration in Wine. By G. Papasogli (*L'Orosi*, **14**, 37—47).—If a thin film of transparent, colourless gelatin is immersed in the sample of wine for 10 to 15 minutes, and dried by pressure between filter paper, it remains colourless if the wine is genuine, but acquires a distinctive tint if any artificial colouring matter is present. When the stained films are treated with sodium carbonate, stannous chloride, or copper acetate, they undergo further changes of colour by which the common dyes may be distinguished from each other. The presence of small quantities of coal-tar colours may be readily detected by this method, which, however, is less sensitive to colouring matters of vegetable origin. For the latter, the following method is proposed:—2 or 3 c.c. of a 10 per cent. solution of lead nitrate is added to 15 c.c. of the wine, the mixture filtered, and the precipitate on the filter covered with the solution of lead nitrate; when this has run through, it is treated on the filter with 6 to 8 c.c. of a saturated solution of borax. A turbid filtrate passes through, which yields a colourless solution on refiltration if the wine is either pure or only contains extract of logwood or brazilwood, or very small quantities of extract of hollyhock (*Althea rosĕa*) or of bilberry (*Vaccinium mirtillus*). An addition of 15 c.c. of the borax solution is also made to the wine filtered off from the lead nitrate; the liquid, after separation of the precipitate, remains colourless if the wine is pure, or only contains the colouring matters just mentioned.

Logwood and brazilwood are specially tested for by agitating 10 to

15 c.c. of wine with dilute sulphuric acid (2 c.c.) and manganese dioxide (4 grams), filtering, and treating the straw-coloured filtrate with stannous chloride. If the above-mentioned dyes are present, the liquid becomes red. The presence of the colouring matter of hollyhock or bilberry is detected by comparing the colour of a mixture of 10 c.c. of the sample and 90 c.c. of a solution of sodium hydrogen sulphite with that of 10 c.c. of a pure wine of the same depth of colour as the sample and 90 c.c. of sulphite. The presence of the adulteration is indicated by a diminution in the intensity of the colour. Full tables are given for the discrimination of the colours absorbed by the gelatin, and of the colours produced in the boracic liquids in cases of sophistication. S. B. A. A.

Assay of Indigo. By F. Voeller (*Zeit. ang. Chem.*, 1891, 110—111).—Processes based on oxidation with potassium permanganate; hydrochloric acid and chloride of lime; sulphuric acid and potassium dichromate, &c., do not give satisfactory results, as commercial indigo usually contains other organic matters (oxalic acid has even been employed as an adulterant); besides it is a very difficult matter to properly notice the end-reaction when titrating. The same foreign matters also interfere with the accuracy of reduction processes, such as Pugh's, with ferrous sulphate and sodium hydroxide, or Fritsche's, with glucose, alkali, and alcohol, where the object is to reduce the indigo-blue to indigo-white, and to finally reoxidise this to the blue compound. Berzelius found that, besides indigo-blue and some mineral matter, the commercial product contains three other substances, which he called indigo-gluten, indigo-red, and indigo-brown. The first, which is soluble in dilute acids, bears some resemblance to vegetable caseïn, and is precipitated from its solution by alcohol and tannin. The second, which is mostly met with in samples prepared by the lime process, is soluble in alkalis, whilst the third is soluble in hot alcohol. Berzelius' process for the assay of commercial indigo is to first extract the sample with hydrochloric or acetic acid, then with alkali, and finally with hot alcohol and water, when a fairly pure indigo-blue will be obtained. The author has improved the process by estimating the nitrogen in the purified product by Kjeldahl's method, and calculating from this the percentage of pure indigo-blue, by multiplying by the factor 9·36. After verifying the accuracy of the process on a sample of sublimed indigo, he analyses the crude product as follows:—The washings with acid, soda, alcohol, and hot water are performed in a perforated platinum crucible, closed with asbestos, and connected with a filter pump. The asbestos containing the indigo-blue is then boiled with sulphuric acid and a drop of mercury, and the ammonia so produced estimated as usual.

L. de K.

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ERRATA.

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Page	Line			
1002	11	from bottom,	*for*	"$(C_5NH_3Me)_2,H_2PtCl_6$" *read* "$(C_5NH_3Me_2)_2,H_2PtCl_6$."
1118	13	,, top	,,	"isomerides" *read* "isomeride."
1163	20	,, ,,	,,	"Malic orthotoluidide" *read* "Malic orthotoluil."
,,	2	,, bottom,	,,	"Malic β-naphthalide" ,, "Malic β-naphthil."
1273	5	,, ,,	,,	"ketones" *read* "ketoximes."
1403	5	,, top	,,	"$2H_2O$" ,, "H_2O."

Vol. LX (Abstr., 1891).

32	5	from bottom,	*for*	"−61·1" *read* "−61·4."
,,	4	,, ,,	*delete*	"approximate."
,,	,,	,, ,,	*for*	"+11·6" *read* "+14·0."
,,	bottom		,,	"−51·2" ,, "−50·8."
43	21	,, top,	,,	"**Glyconic**" *read* "**Gluconic.**"
45	20	,, bottom,	,,	"**Cumine**" ,, "**Cumene.**"
56	bottom,		,,	"*Hippurylbenzalhydrazine*" *read* "*Hippurylhydrazine.*"
105	10	,, bottom,	,,	"STOCKLASA" *read* "STOKLASA."
202	bottom,		,,	"alutamine" ,, "glutamic acid."
207	3	,, top,	,,	"phenyltoluylpentane" *read* "phenyltoluylpropane."
,,	20	,, ,,	,,	"Duismore" *read* "Dinsmore."
,,	11	,, bottom,	,,	"αβ-phenylmetatoluylpropane" *read* "αβ-phenylparatoluylpropane."
301	7	,, top,	,,	"hydroxyazobenzene" *read* "hydroxyazoxybenzene."
353	18	,, ,,	,,	"these plants" *read* "peas."
377	9	,, bottom,	*insert*	"oxalate" *after* "diisobutylamine."
519	26	,, top,	*for*	"**Heat of capacity**" *read* "**Heat capacity.**"
540	9	,, bottom,	,,	"*Chlorethylidine*" *read* "*Chlorethylidene.*"
587	9	,, top	,,	"MAGALHÃES" *read* "MAGALHAẼS."
653	26	,, bottom,	,,	"J. BEVAD" *read* "I. BEWAD."
676	top,		,,	"*Lutidonecarboxylic acid*" *read* "*Lutidonedicarboxylic acid.*"
700	2	,, top,	,,	"*metahydrobenzylazoximethenyl*" *read* "*metahydroxybenzenylazoximethenyl.*"
748	13	,, ,,	,,	"benzene" *read* "benzoïn."
749	25	,, bottom, *et seq.*,	*for*	"tropinic acid" *read* "tropic acid."
777	10	,, ,,	,, ,,	"carbonic oxide" *read* "carbonic anhydride."
777	bottom,		*for*	"gas" *read* "steam."
828	21	,, top,	,,	"*Methyacrylic*" *read* "*Methacrylic.*"

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Page	Line				
870	6	from	top,	*for*	"his own" *read* "his own*" *and insert* footnote "* Lewkowitsch has replied to this criticism in *J. Soc. Chem. Ind.*, **9**, 842; see this vol. p. 511, line 8 *et seq.*"
905	12	,,	,,	,,	"*Tetrachlorotetrethoxyquinonehydrone*" *read* "*Tetrachlorotetrethoxyquinhydrone.*"
918	3	,,	bottom,		The formula for ellagotannic acid should *read* "$C_6H_2(OH)_3\cdot CO\cdot O\cdot O\cdot C_6H_2(OH)_2\cdot COOH$."
946	20	,,	top,	*for*	"[2] **29**" *read* "**229**."
955	24	,,	bottom,	,,	"G. Brissi" *read* "G. Briosi."
962	20	,,	,,	,,	"F. Hofmeister" *read* "E. Ludwig and E. Tillner."
989	top,			,,	"hypertungstates" *read* "pertungstates."
,,	2	,,	top,	,,	"hypermolybdates" ,, "permolybdates."
999	13	,,	,,	,,	"$C_nH_{2n+2}O_2$" *read* "$C_nH_{2n-2}O_2$".
1213	20	,,	bottom,	,,	"*Methylrosiudulone*" *read* "*Methylrosindulone.*"
1287	5	,,	top,	,,	"phenylylucosazone" *read* "phenylglucosazone."
1312	23	,,	,,	,,	"$C_4H_6NaO_4$" *read* "$C_4H_9NaO_4$."
1313	12	,,	,,	,,	"$C_3H_2O_2$" *read* "$C_6H_2O_2$."
,,	19	,,	,,	,,	"27" *read* "20·7."
1315	14	,,	bottom,	,,	"418·6" *read* "+18·6."
1346	26	,,	top	,,	"*Metanitrodioxytri-*" *read* "*Metanitrodihydroxytri-.*"
1417	8 and 9	,,	bottom,	,,	"a new gaseous compound, *phosphorus sulphofluoride*, PF_3S" *read* "a gaseous compound, thiophosphoryl fluoride, PF_3S (see Thorpe and Rodger, Trans., 1888, 766; and 1889, 306)."
1480	4	,,	top,	,,	"*Parahomobenzhydrylaminethiocarbamide*" *read* "*Parahomobenzhydrylthiocarbamide.*"
1522	15	,,	,,	,,	"J. Moitessier" *read* "G. Moitessier."
1535	Table.				The calcium nitrate was added to pot 10 *only*, the ammonium sulphate to pot 12 *only*; pots 9 and 11, as stated in the text, were control pots to which nothing was added.

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